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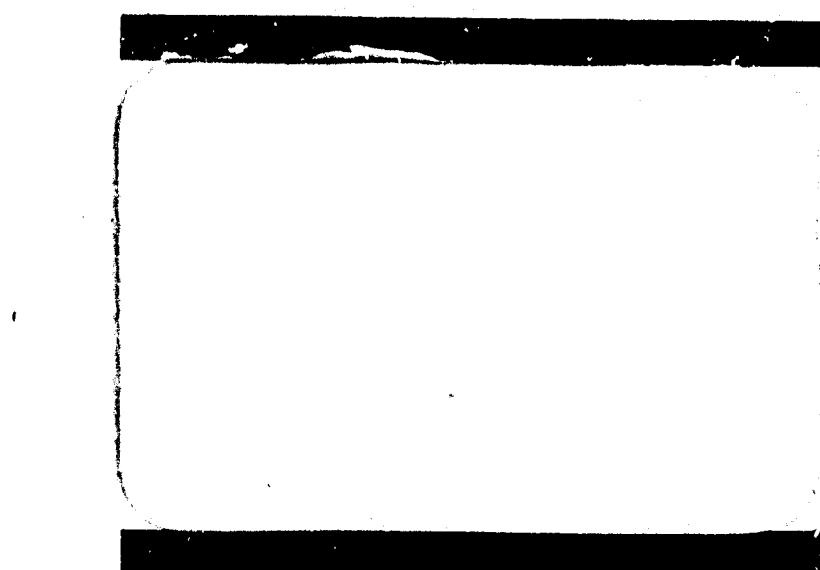
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Report No. ERR-AN-196

AN EVALUATION OF THE  
MECHANICAL PROPERTIES OF ADHESIVES  
AT CRYOGENIC TEMPERATURES AND THEIR  
CORRELATION WITH MOLECULAR STRUCTURE

J. Hertz  
Materials Research

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September 1962

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CONTENTS

<b>List of Illustrations</b>	<b>v</b>
<b>List of Tables</b>	<b>vii</b>
<b>Acknowledgment</b>	<b>ix</b>
<b>Introduction</b>	<b>xi</b>
<b>Abstract</b>	<b>xiii</b>
<b>1. EXPERIMENTAL PROCEDURE</b>	<b>1</b>
<b>2. DISCUSSION OF RESULTS</b>	<b>5</b>
<b>3. CONCLUSIONS</b>	<b>37</b>
<b>References</b>	<b>39</b>
<b>Bibliography</b>	<b>41</b>

# GENERAL DYNAMICS | ASTRONAUTICS

## ILLUSTRATIONS

1. Effect of surface preparation on the tensile-shear strength of Metlbond 406.	6
2. Tensile-shear strength of Metlbond 406 vs. loading rate.	7
3. Effect of thermal cycling on the room-temperature tensile-shear strength of Metlbond 406.	8
4. Effect of specimen width on the tensile-shear strength of Metlbond 406.	9
5. Tensile-shear strength of Metlbond 406 vs. temperature with various plastic adherends.	10
6. Effect of various surface preparations on the tensile-shear strength of FM-1000.	11
7. Tensile-shear strength of AF-41 and Tacky AF-41 vs. temperature.	12
8. Tensile-shear strength of Metlbond 409 (Tacky) vs. temperature.	13
9. Tensile-shear strength of Narmco 3170-7133 (X-284) vs. temperature.	14
10. Tensile-shear strength of various epoxy-polyamide adhesives vs. temperature.	15
11. Effect of resin's molecular weight on tensile-shear strength.	17
12. Total linear thermal expansions reported by NBS Cryogenics Engineering Laboratory.	18
13. Ultrasonic test equipment for determination of adhesive modulus properties.	19
14. Total linear thermal expansion of some adherends.	20
15. Total linear thermal expansion of some adhesive systems.	21
16. Total linear thermal expansion of adhesives and adherends tested at Astronautics.	22
17. Tensile-shear strength of Coast Pro-Seal 777 vs. temperature	23

## GENERAL DYNAMICS | ASTRONAUTICS

18. Static and dynamic tensile-shear strengths of adhesives tested at Hughes Aircraft Co.	24
19. Butt-tensile strength of various adhesives vs. temperature.	25
20. Impact strength of various adhesives vs. temperature.	26
21. Pi-tension tests of sandwich panels having titanium faces and fiberglass core.	27
22. Pi-tension tests of sandwich panels having stainless steel faces and fiberglass core.	28
23. Shear properties of honeycomb panels bonded with Metlbond 406.	29
24. Spectrum of Metlbond 406.	33
25. Spectrum of AF-41.	33
26. Spectrum of FM-1000.	33
27. Spectrum of AF-40.	33
28. Spectrum of Resiweld No. 4, Component A.	34
29. Spectrum of Resiweld No. 4, Component B.	34
30. Spectrum of Narmco 3135, Component A.	34
31. Spectrum of Narmco 3135, Component B.	34
32. Spectrum of Metlbond 4041.	35
33. Spectrum of AF-32.	35
34. Spectrum of APCO 1219.	35

GENERAL DYNAMICS | ASTRONAUTICS

TABLES

I. Surface preparations.	2
II. Young's modulus of Metlbond 406 obtained by tensile-testing of molded specimens.	16

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The author wishes to express his appreciation to the many individuals who were involved in the program to evaluate adhesives at cryogenic temperatures. The efforts of Mr. J. L. Percy in constructing the ultrasonic test equipment and the efforts of Mr. M. D. Campbell in determining the thermal expansion properties of a series of adhesives and adherends is gratefully acknowledged. In addition, the author thanks the many technicians who were instrumental in bonding and testing the test specimens.

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## INTRODUCTION

The Materials Research Group at General Dynamics|Astronautics, A Division of General Dynamics Corporation, conducted a Research Engineering Authorization (REA) program in 1961 entitled, "An Evaluation of the Mechanical Properties of Adhesives at Cryogenic Temperatures and Their Correlation With Molecular Structure." This was a continuation of REA Program No. 111-9106 which was accomplished in 1960. The objectives of this program were to obtain mechanical and physical property data on various basic classes of structural adhesives over the temperature range of -423° to 78°F, and to try to correlate this data within the molecular structure of the adhesive systems.

Since Astronautics began this work in 1960, many other organizations have entered into testing of adhesives at cryogenic temperatures. This increase in testing has resulted primarily from the awarding of major space contracts (Saturn S-IV, Saturn S-II, and Saturn S-I-B). Each of these vehicles requires the use of cryogenic propellants. In addition, small research contracts have been awarded by the National Aeronautics and Space Administration in this area. Data which has been generated by other organizations, and which is available, has been included in this report. Where the data generated by other sources is too extensive to be included, it has been referenced wherever applicable. An up-to-date survey of all literature available on the properties of adhesives at cryogenic temperatures is listed in the Bibliography. Because many of the designs generated for various stages of Saturn required the use of honeycomb structure, a large effort was placed on evaluating bonded honeycomb structures. Although it was not the initial intention of this REA to evaluate composite structures, it was found that this type of data was more important for present design considerations than the normal mechanical property tests on metal-to-metal joints.

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## ABSTRACT

Tensile-shear, butt-tensile, and impact tests were run on a series of adhesives from -423° to 78° F. Pi-tension, plate-shear, and fatigue tests were run on a series of sandwich honeycomb panels having stainless steel and titanium faces, fiberglass honeycomb core, bonded with epoxy-nylon and filled epoxy-phenolic adhesives. The effect of primers, cleaning cycles, thermal cycling, and loading rates on the tensile-shear strength of adhesives was determined at cryogenic temperatures.

Thermal expansion and tensile testing was conducted on molded and cast adhesives from -423° to 78° F. Infrared curves were run on the adhesives evaluated in this Research Engineering Authorization (REA) report, as well as those evaluated in REA 111-9106.

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## 1

### EXPERIMENTAL PROCEDURE

Tensile-shear (1/2-in. overlap) coupons were machined and fabricated from the following materials: 0.020-in. EFH 301 stainless steel, 0.020-in. 5Al-2.5Sn titanium alloy, and 0.125-in. Conolon 522 (epoxy-fiberglass laminate). The lap-shear coupons were prepared by bonding 4 in.  $\times$  1 in. strips to obtain an over-all test specimen of 7-1/2 in.  $\times$  1 in. The ends of the specimens contained either spot-welded or bonded doublers for reinforcement in the grip areas and 1/2-in. holes for accommodating pin-type grips.

Butt-tensile coupons were prepared from 3/4-in. round stock 321 stainless steel. After bonding, the coupon had an over-all length of 2 in. and a bond area of 0.442 sq.in. The coupons were threaded on each end with a 3/4-10 thread.

Impact specimens were prepared from 321 stainless steel flat stock per Federal Test Method Standard No. 175 (Tentative Standard Method 1051.1-T). They consisted of two stainless steel blocks (1 in.  $\times$  1 in.  $\times$  3/8 in. and 1-3/4 in.  $\times$  1 in.  $\times$  3/4 in.) bonded together and resulting in 1 sq. in. of bonded area.

Pi-tension specimens were made per Fort Worth Specification (Reference 1)\*. Faces were either 0.032 in. EFH 301 stainless steel or 0.050 in. 5Al-2.5Sn titanium alloy and were bonded to 1/2-in. thick Hexcel NRP-3/16 in. core of 5.5-5.7 lb./cu.ft. (pcf) density. Specimens are 2-in. dia. discs and hence have a bond area of  $\pi$  (3.14) sq.in.

Plate-shear specimens were made per MIL-STD-401A. The specimens were 5.670 in.  $\times$  2 in. and had faces of 0.032-in. EFH 301 stainless steel which were bonded to 1/2-in. thick Hexcel HRP-3/16 in. core of 5.7 pcf density.

Surface preparation of all metal-to-metal test coupons was standardized for each adherend (see Table I). The effects of surface preparation on tensile-shear strength was evaluated for stainless steel adherends; therefore, more than one etch procedure was utilized in bonding the stainless steel overlap joints. Priming and bonding were

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\*References are listed on Page 39.

# GENERAL DYNAMICS | ASTRONAUTICS

Table I. Surface preparations.

## STAINLESS STEEL & TITANIUM ADHERENDS

1. (ASTRONAUTICS ETCH) WIPE SPECIMENS WITH TRICHLOROETHYLENE. IMMERSE SPECIMEN FOR 10 MIN. AT 150°F IN THE FOLLOWING SOLUTION:

100 GM HYDROCHLORIC ACID (CONC.)

4 GM HYDROGEN PEROXIDE (30%)

20 GM FORMALDEHN (40%)

90 GM WATER

RINSE SPECIMENS IN COLD TAP WATER. FOLLOW THIS WITH A DISTILLED WATER RINSE & AIR DRY. THIS IS FOLLOWED BY 5 TO 10 MIN. OF ETCH AT 140-160°F IN THE FOLLOWING SOLUTION:

100 GM SULFURIC ACID (CONC.)

10 GM SODIUM DICHROMATE

30 GM WATER

REPEAT RINSE AND DRYING PROCEDURES AS ABOVE.

2. WIPE SPECIMENS WITH TRICHLOROETHYLENE. IMMERSE SPECIMENS FOR 5 TO 10 MIN. AT 200°F IN THE FOLLOWING SOLUTION:

283 GM PREBOND 700

1 GAL. WATER

RINSE SPECIMENS IN COLD TAP WATER. FOLLOW THIS WITH A DISTILLED WATER RINSE & AIR DRY.

3. SAME AS FIRST PROCEDURE EXCEPT USE 300 GM WATER IN SECOND ETCH SOLUTION.

## ALUMINUM ADHERENDS

WIPE SPECIMENS WITH TRICHLOROETHYLENE. IMMERSE SPECIMENS FOR 10 MIN. AT 150°F IN THE FOLLOWING SOLUTION:

30 GM WATER

10 GM SULFURIC ACID (CONC.)

4 GM SODIUM DICHROMATE

RINSE SPECIMENS IN COLD TAP WATER. FOLLOW THIS WITH A DISTILLED WATER RINSE & AIR DRY.

## PLASTIC LAMINATE ADHERENDS

SAND LIGHTLY & WIPE CLEAN WITH TRICHLOROETHYLENE.

accomplished according to manufacturer's recommendations. Pi-tension and plate-shear coupons were not etched prior to bonding. Tensile-shear specimens were loaded at a rate of 600 to 700 psi of the shear area per minute (ASTM D 1002-52T) except when evaluating the effect of loading rate on lap-shear strength. The butt-tensile coupons were loaded at 350 lb./min. (ppm); the pi-tension specimens were loaded at both

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500 and 4,000 ppm: and the plate-shear specimens were pulled at 0.0285 in./min. head travel. Impact specimens were broken using a hammer velocity of 17 fps.

The tensile-shear, butt-tensile, pi-tension, and plate-shear specimens were tested using a 50,000-lb. Baldwin-Emery SR-4 Testing Machine, Model FGT, and a 30,000-lb. Tinius Olsen electromatic testing machine. Impact specimens were tested using a Sonntag Universal impact machine, Model SI-1P. The proper temperature environment was provided by immersing the specimen in alcohol and dry ice (-100°F), liquid nitrogen (-320°F), or liquid hydrogen (-423°F). Details of the experimental procedure including temperature measurement, liquid level indication, and safety precautions are given in a paper by Christian and Watson (Ref. 2).

Alignment fixtures (Ref. 3) were utilized for bonding of the tensile-shear, butt-tensile and impact specimens. Spherical joints were utilized in the tensile-testing machines to ensure alignment during testing. Prior to test the tensile-shear coupons were measured optically to determine the length and width of the overlap area. Thickness measurements of the adherends and the bonded area for each specimen were made with a micrometer to determine the adhesive thickness of each test coupon. After testing, all specimens that failed in the bonded area rather than in the adherends were visually examined. The type and extent of each type of failure was noted. For this report a cohesion failure is defined as one that occurs within the adhesive, while an adhesion failure is defined as one that occurs in a weak boundary layer. In the cases where a primer was utilized and failure occurred between adhesive and primer, the failure is considered to be one of adhesion. In the cases where the adhesive is a supported system and failure occurs between the resin and the reinforcement, the failure is considered to be one of cohesion.

Thermal expansion specimens were machined out of molded or cast adhesives. These specimens were tested utilizing a modified Leitz dilatometer and a thin-sheet, quartz tube dilatometer. The modified Leitz dilatometer results in a continuous temperature vs. expansion curve, whereas the thin-sheet dilatometer was used only for obtaining the total linear thermal expansion of the specimens over a selected temperature range.

Infrared curves on the adhesives were run on a Perkin-Elmer Model 21 double-beam infrared spectrophotometer. Specimens of the unsupported film systems were prepared by stretching or heat-pressing of the tapes between sheets of Teflon in order to obtain specimens thin enough for infrared study.

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## 2

### DISCUSSION OF RESULTS

Tensile-shear testing at cryogenic temperatures was initiated in REA 111-9106 and continued in 1961. The tensile-shear testing was primarily concerned with determining the effects of various parameters on tensile-shear strength. The parameters evaluated included surface preparation, loading rate, thermal cycling, and specimen width.

Figure 1 indicates the effect of surface preparation of the adherends on the tensile-shear strength of Metlbond 406. The adherend utilized for this program was 0.020-in. EFH 301 stainless steel. Metlbond 406 was selected for additional evaluation since it had resulted in the highest strengths at cryogenic temperatures when tested in 1960. Values obtained with the Astronautics concentrated chromate etch were reported in ERR-AN-032. Two other etching cycles were examined this year. The Forest Products Laboratory's stainless steel etch (see Table I) is identical to the first part of the Astronautics etch but is followed by a dilute chromate rather than a concentrated chromate etch. The FPL etched specimens when tested at -423°F failed at approximately 70% of the tensile-shear strength obtained with the Astronautics etch. The use of an epoxy-nylon primer (Bloomingdale Rubber Co. FM-1009-8), in conjunction with the Astronautics etch, resulted in strengths approximately 50% lower than those obtained when no primer was utilized. This confirms the testing of primers accomplished in the initial REA. The use of an alkaline surface preparation (Bloomingdale Rubber Co. Pre-Bond 700) resulted in an average tensile-shear strength at -423°F, approximately 7% higher than those obtained with the Astronautics etch. It should be pointed out, however, that the batch of Metlbond 406 utilized in the 1960 program was different from the one utilized in evaluating the FPL stainless steel etch, Pre-Bond 700, and FM-1009-8. There may be a drastic difference in tensile-shear strength obtained with one batch of adhesive from that obtained with another batch. This phenomenon has been evident in tests conducted at higher temperatures by Narmco Research and Development, and is quite a common occurrence in the testing of adhesives.

Figure 2 indicates the effect of loading rate on the tensile-shear strength of Metlbond 406 joints using 0.020-in. EFH 301 stainless steel adherends. The effect of loading rate was conducted at -320° and -423°F, and covered the range of loading rate

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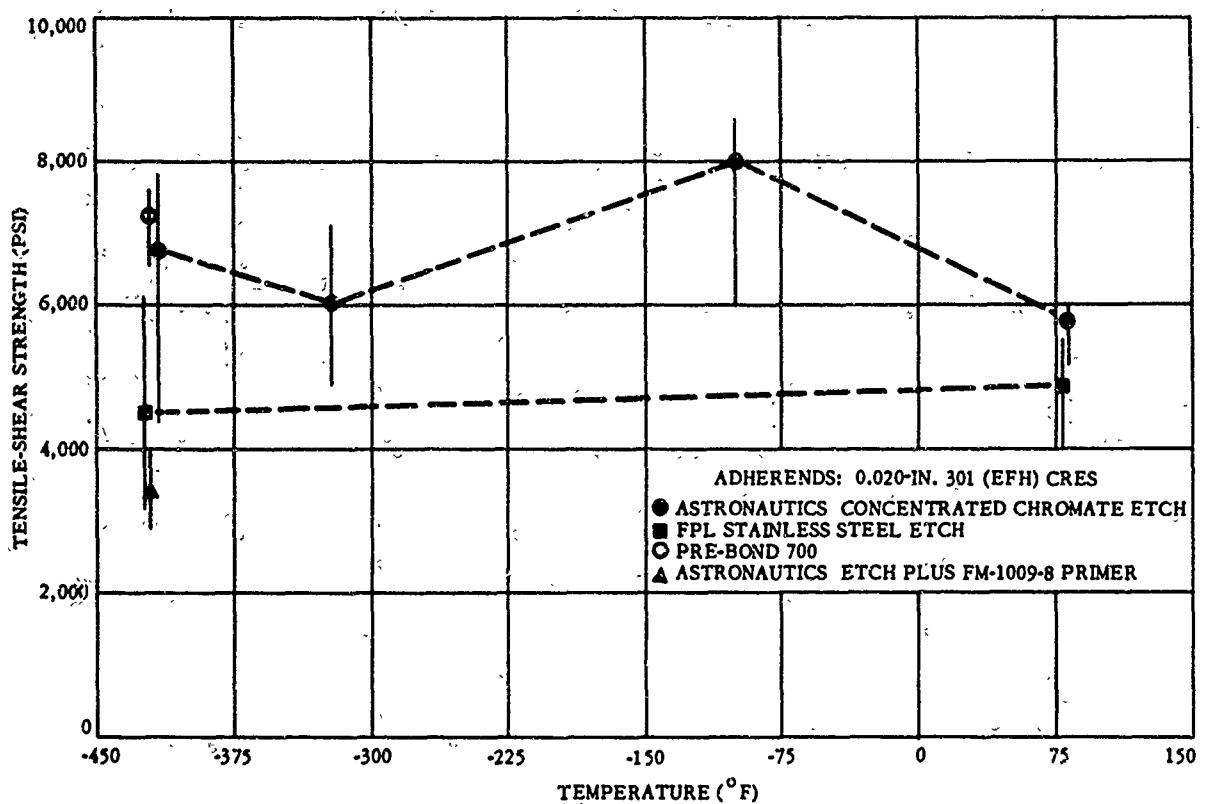


Figure 1. Effect of surface preparation on the tensile-shear strength of Metlbond 406.

from 1,000 to 10,000 ppm. At both temperatures the general trend was a gradual increase in tensile-shear strength with increase in loading rate. There was approximately a 40% increase in tensile-shear strength when specimens were loaded at 10,000 ppm over the strengths obtained when the specimens were loaded at 1,000 ppm.

McClintock and Hiza (Ref. 4) have shown that thermal cycling has a deleterious effect on the tensile-shear strength at room temperature of a filled epoxy adhesive. To determine if this might also be the case with the epoxy-nylon systems, some stainless steel specimens were bonded with Metlbond 406. Five specimens were cycled 10 times between -423° and 78°F, five were cycled 10 times between -320°F and 78°F, and five were cycled 10 times between -100° and 78°F. They were then all pulled at 78°F and compared to specimens which had not been subjected to thermal cycling. Figure 3 is a graphical presentation of the results obtained. It can be seen that there was no appreciable change in tensile-shear strength as a result of thermal cycling.

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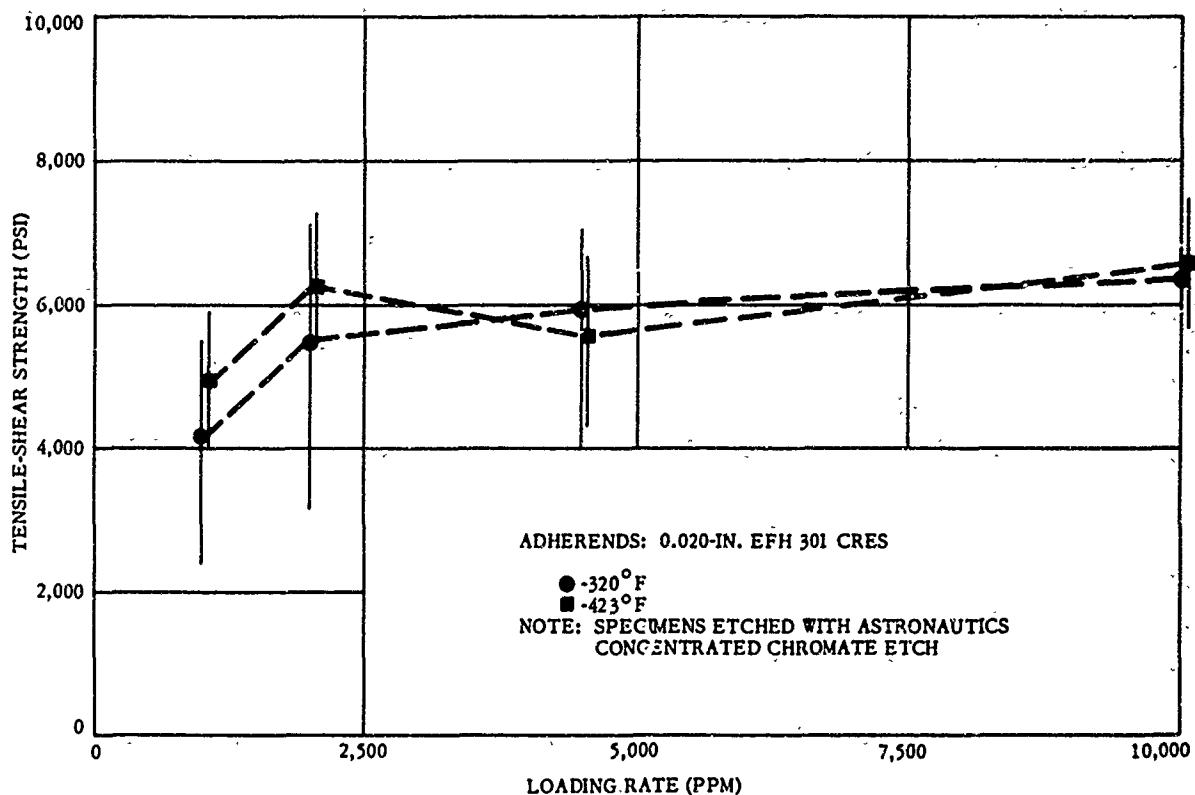


Figure 2. Tensile-shear strength of Metlbond 406 vs. loading rate.

It has generally been accepted that the width of the overlap joint does not affect the strength of the joint. However, testing of specimens 38 in.  $\times$  4 in. wide, having 1/2-in. and 3/4-in. overlap joints bonded with Metlbond 406, resulted in strength values considerably lower than those obtained with the standard specimen 1 in. wide. It was felt that the extreme length of the specimen and the equipment used for holding and loading the specimens might result in some eccentricity in the joints. Tests were repeated at room temperature by Narmco Materials Division, and at room temperature and at -423°F at Astronautics with smaller specimens (8 to 12 in. long). Results are plotted in Figure 4 and seem to verify that joints bonded with Metlbond 406 result in lower strength per unit area with increase in the joint width. It is felt that additional effort is required in this field, both experimentally and analytically, with Metlbond 406 and other adhesive systems.

In REA 111-9106 (Ref. 3), it was determined that when Metlbond 406 was used for bonding tensile-shear specimens having polyester-fiberglass or phenolic-fiberglass

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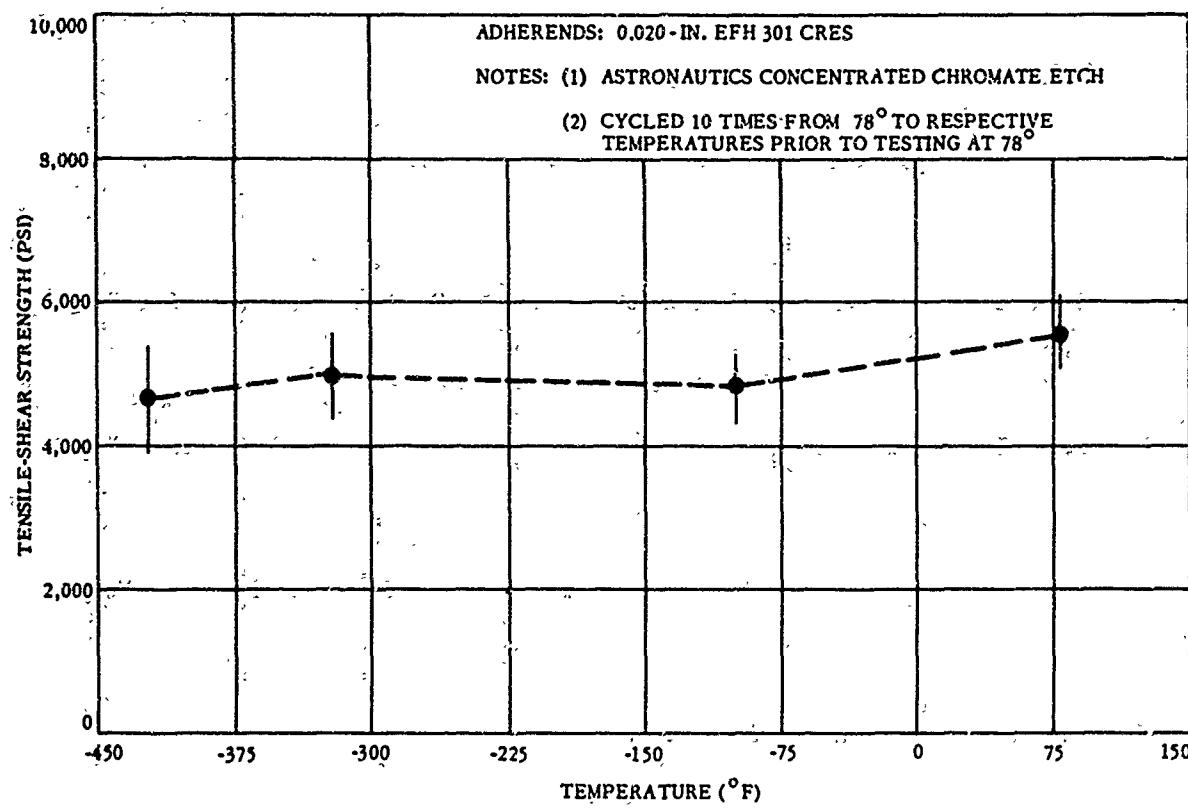


Figure 3. Effect of thermal cycling on the room-temperature tensile-shear strength of Metlbond 406.

adherends, failure always occurred within the adherends rather than in the adhesive. It was felt that a truer value of the joint strength of Metlbond 406 might be obtained by testing laminates which had higher interlaminar shear strength. Figure 5 shows the tensile-shear values obtained when using Conolon 522 (epoxy-fiberglass laminate) adherends. Values obtained previously have also been included for comparison purposes. Once again all failures occurred in the adherends rather than in the adhesive, even though the stress levels at which failure occurred were much higher than those obtained previously.

Figure 6 shows the effect of various surface preparations on the tensile-shear strength of FM-1000 epoxy-nylon adhesive. Since original specimens tested in 1960 had been supplied by Bloomingdale Rubber Co., and because these specimens had uneven glue lines, it was decided to test some specimens bonded at Astronautics. Using the same etch procedure as had been used initially (Astronautics etch), specimens tested at  $-320^{\circ}\text{F}$  resulted in an average tensile-shear strength approximately 30%

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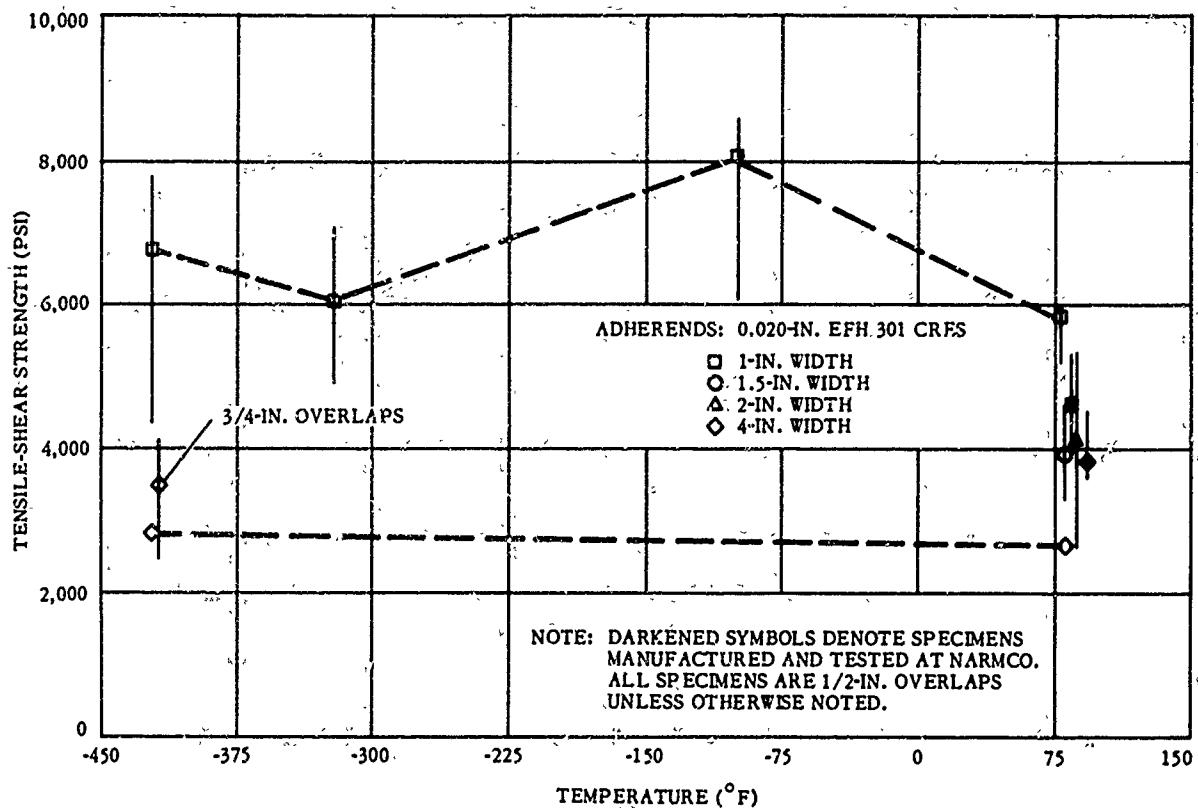


Figure 4. Effect of specimen width on the tensile-shear strength of Metlbond 406.

higher than that obtained in 1960. Specimens prepared with the Astronautics etch and using the FM-1009-8 primer were tested at  $-423^{\circ}\text{F}$  and resulted in values similar to those obtained with the Metlbond 406 joints which had been similarly prepared (see Figure 1). Specimens etched with Pre-Bond 700 once again proved to give the highest strengths with stainless steel adherends at  $-423^{\circ}\text{F}$ .

Figures 7 and 8 show the tensile-shear strengths obtained with two new epoxy-nylon systems: Tacky AF-41 and Tacky Metlbond 409. The advantage of utilizing tacky unsupported tapes is most apparent when bonding large vertical surfaces. With the other unsupported tapes it is necessary to utilize tacking agents, heat tacking, or mechanical means for holding the tape in place during bonding. Bonding is more difficult and there is a possibility of obtaining poor bonds in local areas. Figure 7 indicates that curing temperature is critical when utilizing AF-41. By curing at  $390^{\circ}\text{F}$  instead of  $350^{\circ}\text{F}$  there was approximately a 35% decrease in tensile-shear strength at  $320^{\circ}$  and  $-423^{\circ}\text{F}$ . The values obtained with Tacky Metlbond 409 are extremely promising, and further testing with this adhesive system is indicated.

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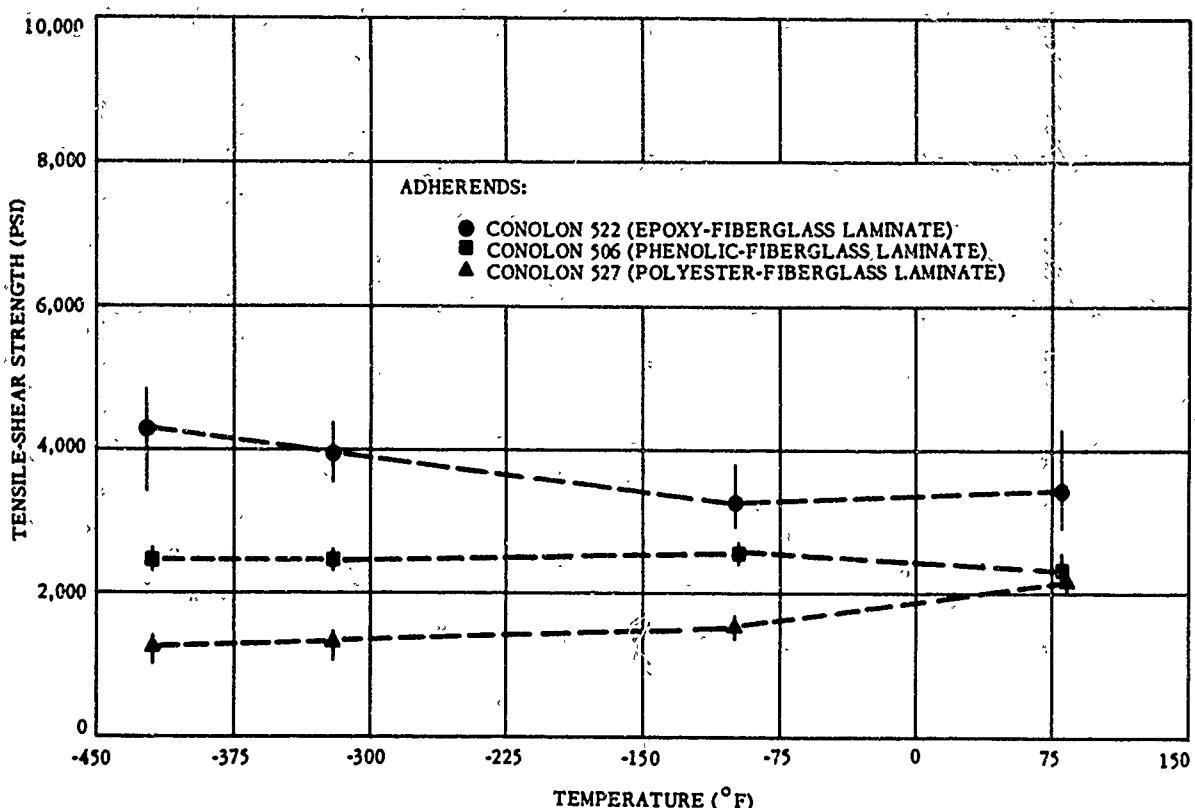


Figure 5. Tensile-shear strength of Metlbond 406 vs. temperature with various plastic adherends.

Because it is advantageous to utilize room-temperature curing adhesives, some effort was placed on evaluating this type of system even though they were definitely inferior to the heat-cured systems. Figure 9 shows the tensile-shear strengths obtained with Narmco 3170-7133 (X-284) adhesive with both 0.020-in. EFH 301 stainless steel and 0.020-in. 5Al-2.5Sn titanium alloy adherends. This system was developed by Narmco Research and Development under NASA contract No. NAS 8-1565, Development of Adhesives for Very Low Temperatures. It consists of Narmco 3135 (epoxy-polyamide system) filled 33% by weight with finely ground nylon. This system, when evaluated by Narmco, resulted in excellent strengths with 7075-T6 aluminum adherends; however, the values obtained at Astronautics with stainless steel and titanium adherends were poor. Tests were run only at -320° and -423°F to conserve funds.

Figure 10 shows the tensile-shear results obtained with various ratios of Epon 828 (epoxy)/Versamid 125 (polyamide). The 50-50 ratio by weight resulted in the highest

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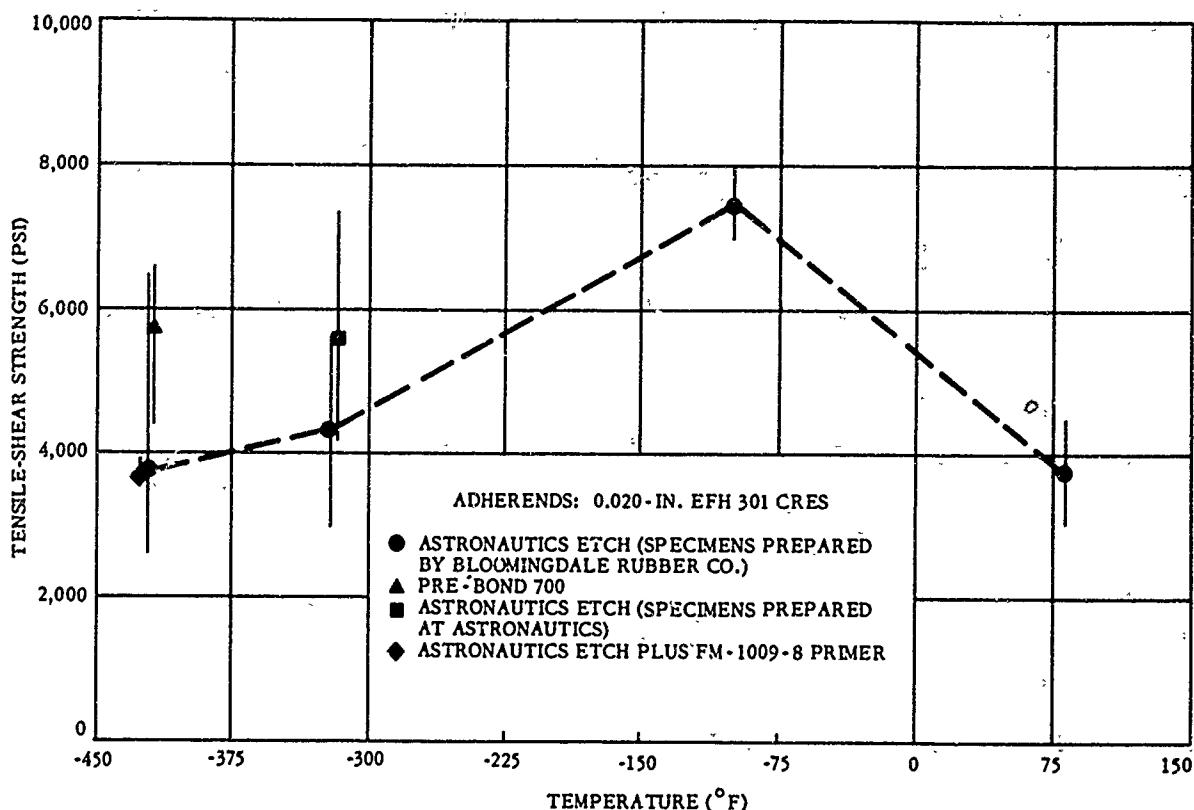


Figure 6. Effect of various surface preparations on the tensile-shear strength of FM-1000.

values. The results previously obtained on Narmco 3135 have also been included on this graph. In most instances, there was a large spread in tensile-shear data. This is more common in room-temperature curing liquid adhesives because it is more difficult to control glue line thickness, mixing of components, gas bubbles in the glue line, etc. Only specimens bonded with Narmco 3135 were tested at -100° and -423°F. It is thought that had the other systems been evaluated at these temperatures they would result in curves similar in shape to that obtained with the Narmco 3135.

Work accomplished by Hiza and Barrick at the Cryogenic Engineering Laboratory of the National Bureau of Standards (Ref. 5) has shown the effect of the molecular weight of epoxy resin on the tensile-shear strength obtained with the cured epoxy system. The epoxy resins checked were derived from the polycondensation of epichlorohydrin and bisphenol-A. Figure 11 shows the tensile-shear values obtained with 0.125-in. 2024 aluminum adherends when the epoxy resins were cured with stoichiometric

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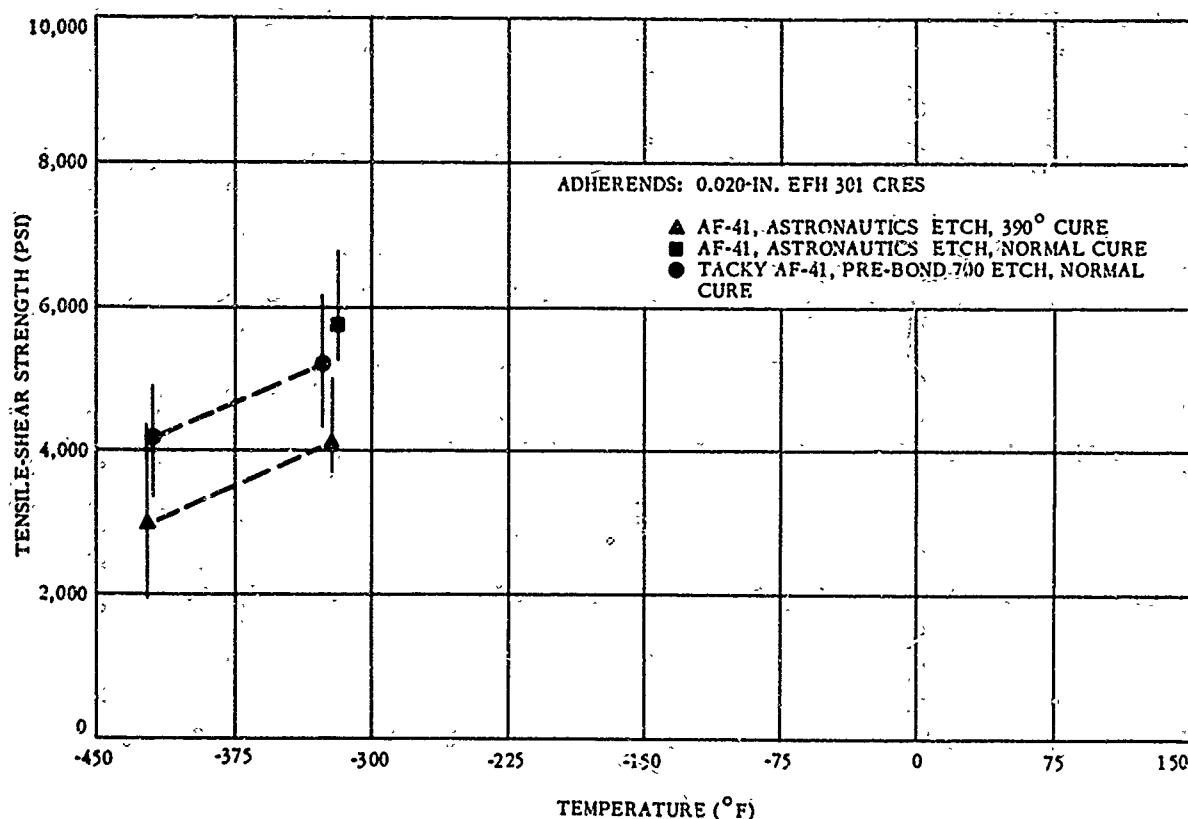


Figure 7. Tensile-shear strength of AF-41 and Tacky AF-41 vs. temperature.

amounts of meta-phenylenediamine. The values obtained at 300°K (81°F) indicate a gradual increase in tensile-shear strength with increase in molecular weight. This same dependence had previously been shown by N.A. de Bruyne (Ref. 6) with aluminum lap joints using phthalic anhydride as a curing agent. At 76°K (-323°F) Hiza and Barrick found that tensile-shear strength increased with molecular weight up to approximately a molecular weight of 700 and then gradually decreased with an additional increase in molecular weight. They postulated that, at 300°K, residual stress in the lap joint was primarily dependent on chemical shrinkage, while at 76°K the residual stress was due primarily to thermal contraction. Figure 12 shows the graphically integrated thermal expansivity of the materials evaluated at NBS. Hiza and Barrick postulated that the uncured resin is absorbed by the adherend and that the adhesive strength is relative to the magnitude of the adsorptive forces; the strength of adsorption of epoxy resins increasing with molecular weight. As the chemical curing reaction progresses, the mobility of the resin molecules is reduced, thus limiting additional adsorption. The cohesive strength is developed as a result of the curing process, forming a tough,

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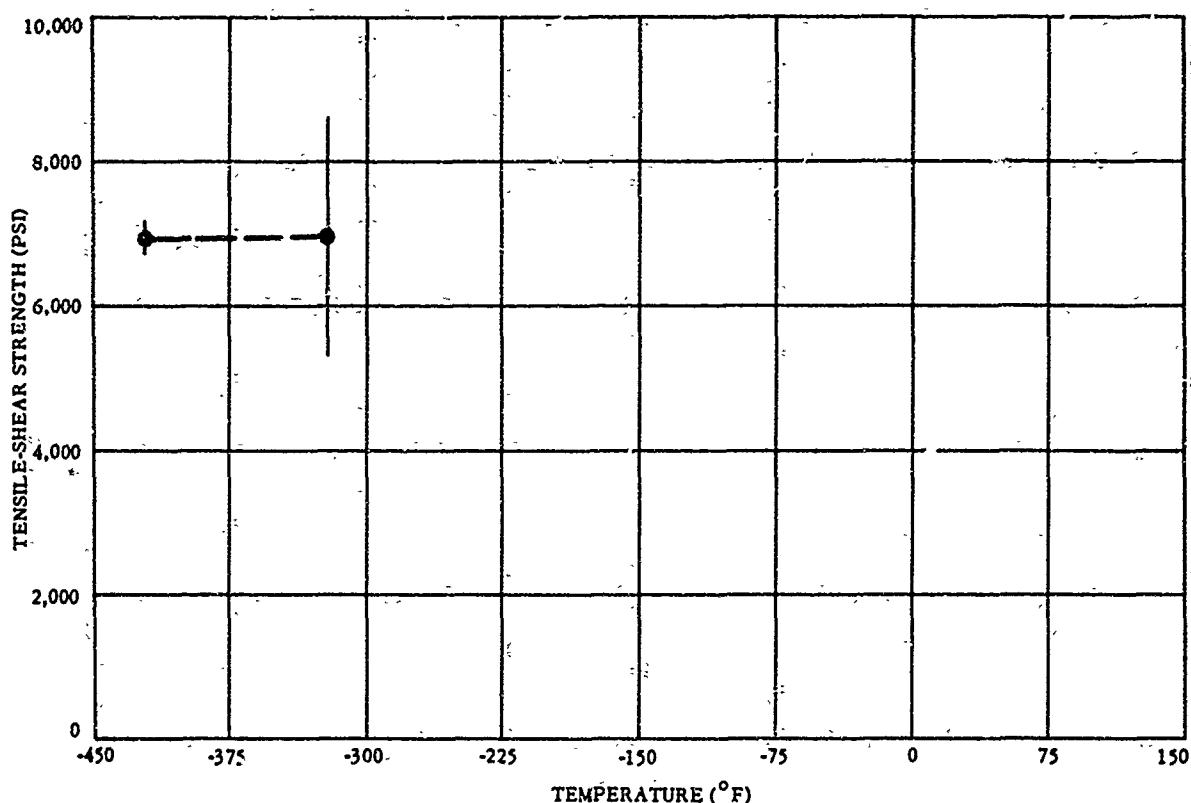


Figure 8. Tensile-shear strength of Metbond 409 (Tacky) vs. temperature.

crosslinked structure. Hiza and Barrick assumed that forces of adsorption increase as the temperature is decreased. Most polymeric materials also tend to increase in cohesive strength at low temperatures, therefore, it would be reasonable to expect tensile-shear bonds at 76°K to be stronger than those at 300°K, provided that residual thermal stresses are not limiting. Because Hiza and Barrick consider the residual thermal stresses to consist of stresses resulting from chemical shrinkage and thermal contraction, the net effect of residual stresses is dependent on the service temperature and the magnitude of thermal contraction of the adherent material. At 300°K the thermal effect is small since the resins were cured at a comparatively low temperature (1 hour at 110°C). At 76°K the differential thermal contraction between adhesive and adherent adds stresses to those already present at 300°K. Looking at Figure 12, one can readily see why the high molecular weight resins suffer the greatest loss in strength.

It should be noted that Hiza and Barrick only considered thermal stresses. This may be misleading because there are a number of other stresses which may be giving

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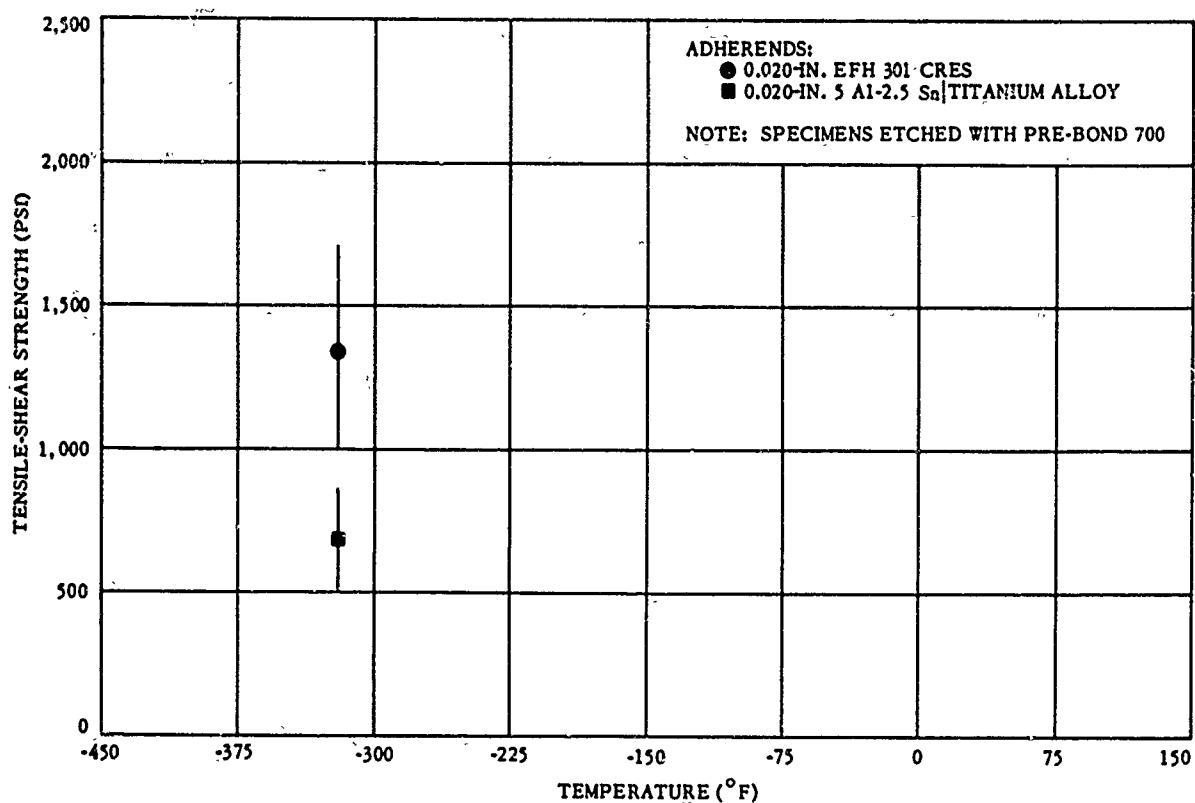


Figure 9. Tensile-shear strength of Narmco 3170-7133 (X-284) vs. temperature.

interactions, and what appears to be a correlation may in fact be far from a correlation. There was no attempt made to determine what is the change in modulus of the adhesives at the different test temperatures. Since each resin system checked would have a different ultimate cohesive strength and a different shear modulus at each of the test temperatures, neglecting these properties and trying to correlate molecular weight to tensile-shear strength by use of thermal stresses alone appears to be oversimplifying the problem.

To obtain a truer picture of the stress concentration resulting in tensile-shear joints, an attempt was made to obtain the mechanical properties as well as the thermal expansion of molded adhesives. The first attempt was to obtain stress-strain curves at the various test temperatures on molded tensile coupons. In addition to being very brittle when tested at  $-320^{\circ}\text{F}$ , the values obtained on the molded adhesives were very inconsistent. To obtain more consistent and useful data an attempt was made to obtain modulus data ultrasonically by modifying a setup which had been developed by Deitz and coworkers at Massachusetts Institute of Technology (Ref. 7). The equipment

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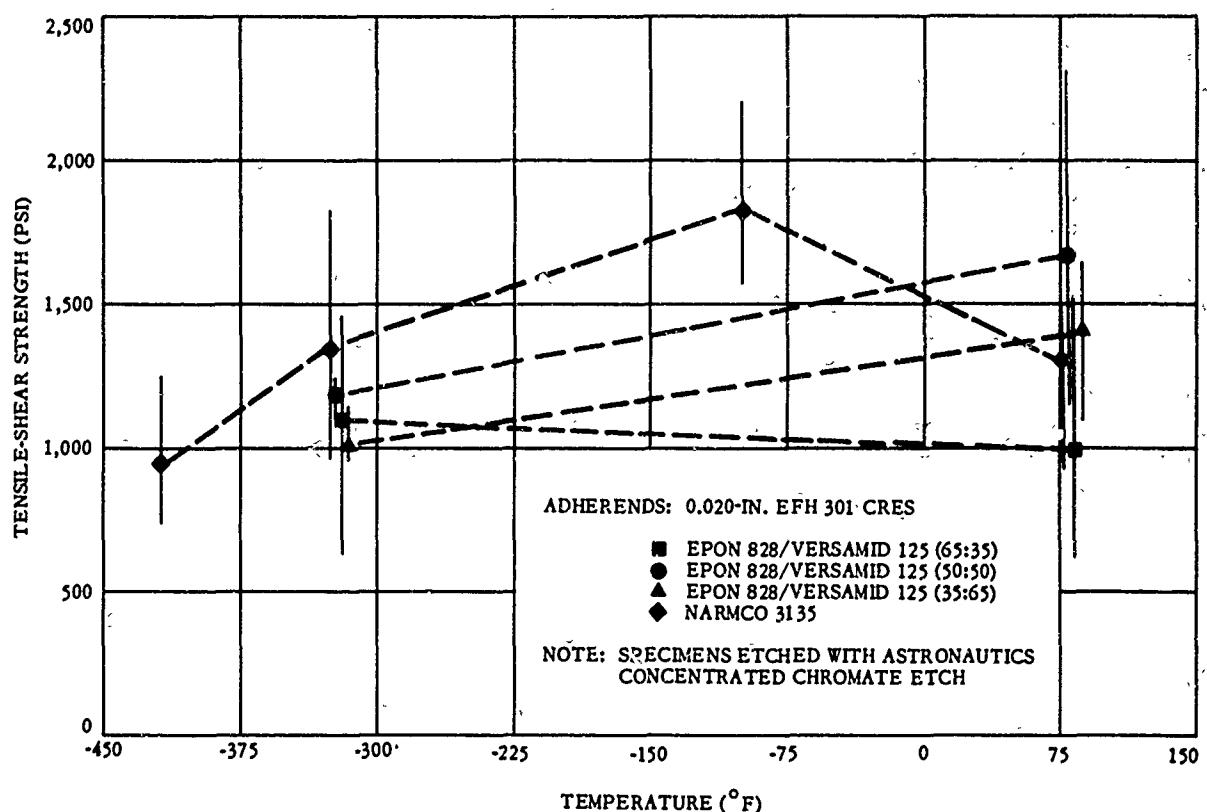


Figure 10. Tensile-shear strength of various epoxy-polyamide adhesives vs. temperature.

(see Figure 13) and specimens to be evaluated have been built, but this REA expired before the work could be completed. The equipment for obtaining the necessary resonance properties, the resonant frequency, and half-power bandwidth, consists of three major parts: a driving system to set up longitudinal ultrasonic vibrations in the specimens, a detecting system to indicate the amplitude of vibrations, and a frequency-measuring system. The specimen consists of a thin adhesive layer joining two cylindrical bars end to end. Relations have been derived by Nolle and Westervelt (Ref. 8) to calculate Young's modulus and viscous modulus knowing the resonance properties of the cemented bar and a continuous bar of the same length and material. Table II contains the modulus data obtained at 78°, -100°, and -320°F when using molded tensile specimens of Metlbond 406.

Total linear thermal expansion vs. temperature curves were run on some typical adherends and adhesives over the temperature range of -200° to +25°C. These curves

# GENERAL DYNAMICS | ASTRONAUTICS

Table II. Young's modulus of Metlbond 406 obtained by tensile-testing of molded specimens.

SPECIMEN NO.	TEMPERATURE (°F)	YOUNG'S MODULUS (PSI)
1	78	43,400
2	78	44,300
3	78	49,000
		AVERAGE 45,600
4	-100	291,000
5	-100	354,000
6	-100	296,000
7	-100	235,000
		AVERAGE 294,000
8	-320	525,000
9	-320	1,177,000
10	-320	810,000
11	-320	866,000
		AVERAGE 770,000

are shown in Figures 14 and 15. Figure 16 shows the total linear thermal expansion of these adhesives and adherends between 76° and 300°K. Examination of this graph seems to indicate that for each individual adhesive system, the highest tensile-shear strengths should be obtained with the 2024-T3 aluminum alloy adherends. The joints utilizing 301 full-hard stainless steel adherends should result in higher strengths than those using 5Al-2.5Sn titanium alloy adherends. In most cases, this order has been followed; however, it should be pointed out that the strength will be dependent on the ability to prepare each of the adherends adequately so that in no case is failure adhesive in nature.

Many of the common sealants and putties act as structural adhesives at cryogenic temperatures. These would be used more frequently for cryogenic adhesive applications if these materials had higher room-temperature adhesive properties. Figure 17 shows some tensile-shear strengths obtained with Coast Pro Seal 777 polyurethane sealant using 0.020-in. EFH 301 stainless steel adherends. The values obtained were considerably lower than those obtained previously by the Applied Manufacturing Research Group (Ref. 9). The discrepancy in results may be a result of two etch procedures. Coast Pro Seal 777 also has been known to be affected by storage conditions and this may account for the large difference in tensile-shear results.

GENERAL DYNAMICS | ASTRONAUTICS

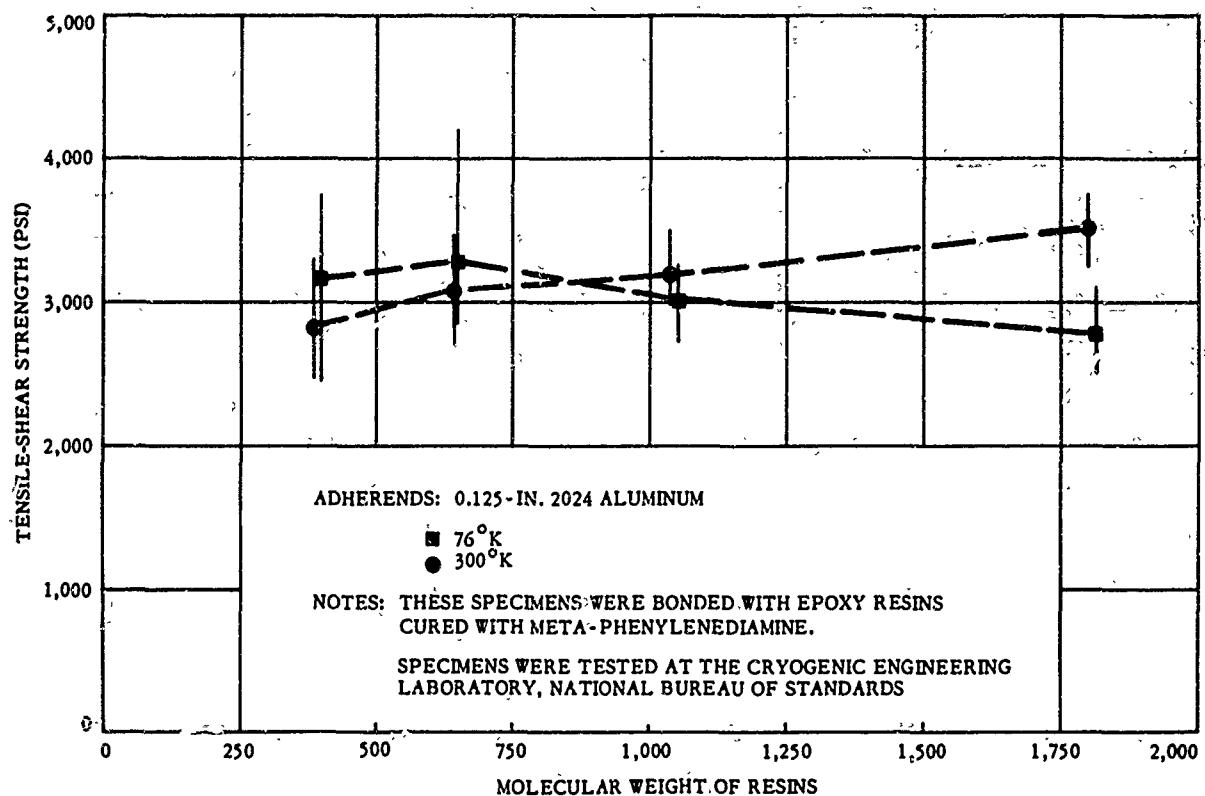


Figure 11. Effect of resin's molecular weight on tensile-shear strength.

Hughes Aircraft Co. has done considerable work in the area of sealants and adhesives at cryogenic temperatures (Ref. 10). Figure 18 shows the static and dynamic shear strengths obtained with DC-731 (silicone sealant) and Metlbond 406. Hughes Aircraft Co. has recently obtained a small research contract from NASA for the development of sealants for low-temperature applications. Progress on this contract (NAS 8-2428) is available, but data is too comprehensive to be included in this report.

In addition to the testing of tensile-shear specimens, a series of butt-tensile tests was also conducted. It can be seen from Figure 19 that the butt-tensile strength of specimens bonded with epoxy-nylon adhesives is considerably higher than the strengths obtained with other classes of adhesives. The values obtained with the butt-tensile coupons are considerably higher than the values obtained with tensile-shear coupons. This would indicate that there is less stress concentration in a butt-tensile specimen than in a tensile-shear specimen. Results obtained with Metlbond 406 at -423°F were more consistent than the values obtained with FM-1000. Examination of the FM-1000 bonded specimens after failure revealed two distinct phases of the adhesive. One phase

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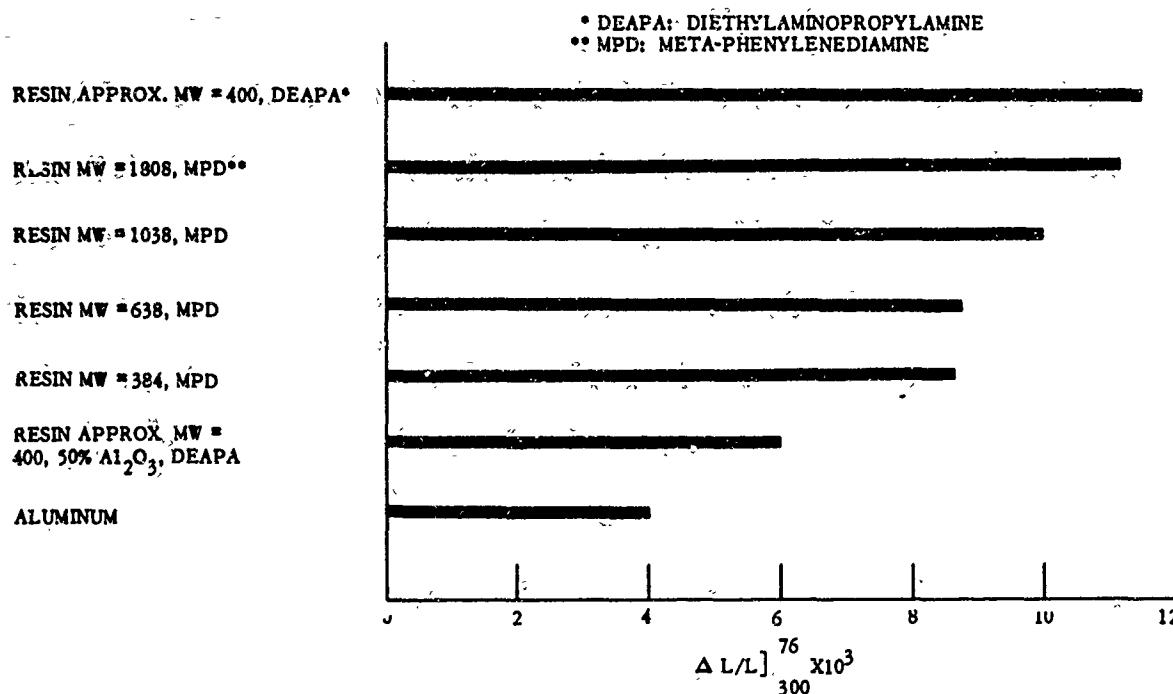


Figure 12. Total linear thermal expansions reported by NBS Cryogenics Engineering Laboratory.

consisted of small glossy pieces of resin. The larger the particle size, the lower the butt-tensile strength. Similar findings were observed when failed tensile-shear coupons bonded with FM-1000 were examined. The order of decreasing strength observed in the butt-tensile tests when testing different classes of adhesives was almost identical to that observed with the tensile-shear coupons (see Ref. 11).

Figure 20 compares the impact strength of a series of adhesives at -320° and 78°F. Once again, the epoxy-nylon adhesives resulted in higher strengths than all the other adhesive systems evaluated. This would indicate that not only are they stronger at cryogenic temperatures, but that they are also considerably tougher. The Metlbond 406 resulted in much higher strengths than the FM-1000, indicating that although they are both epoxy-nylons there is a difference in properties resulting from differences in method of preparation, catalyst, and ratio of components. All impact specimens were tested with a Sonntag tester, using the normal hammer at a head velocity of 17 fps. Initial testing of the Metlbond 406 bonded specimens with a head velocity of 11 fps failed to break the specimens.

GENERAL DYNAMICS | ASTRONAUTICS

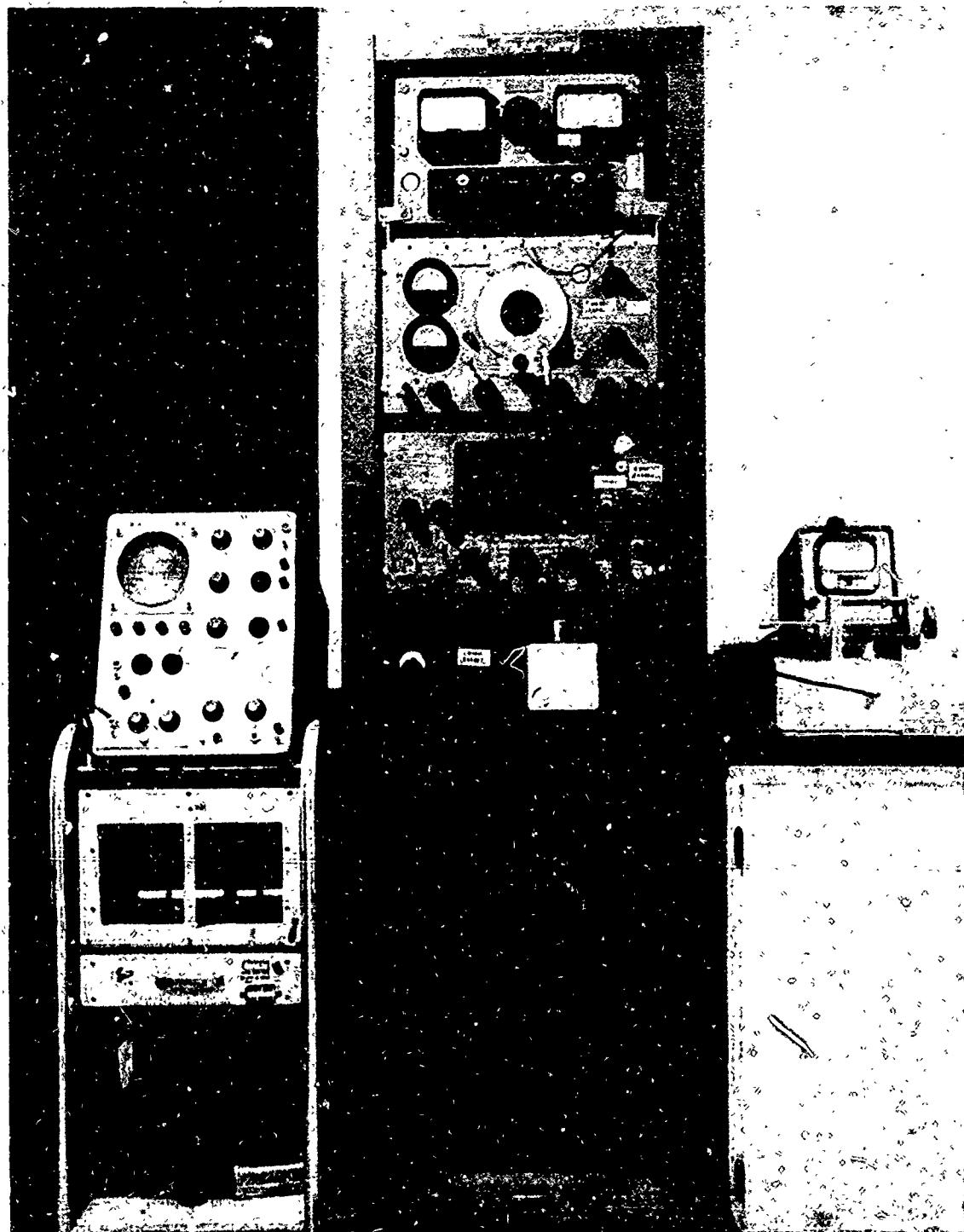


Figure 13. Ultrasonic test equipment for determination of adhesive modulus properties.

GENERAL DYNAMICS | ASTRONAUTICS

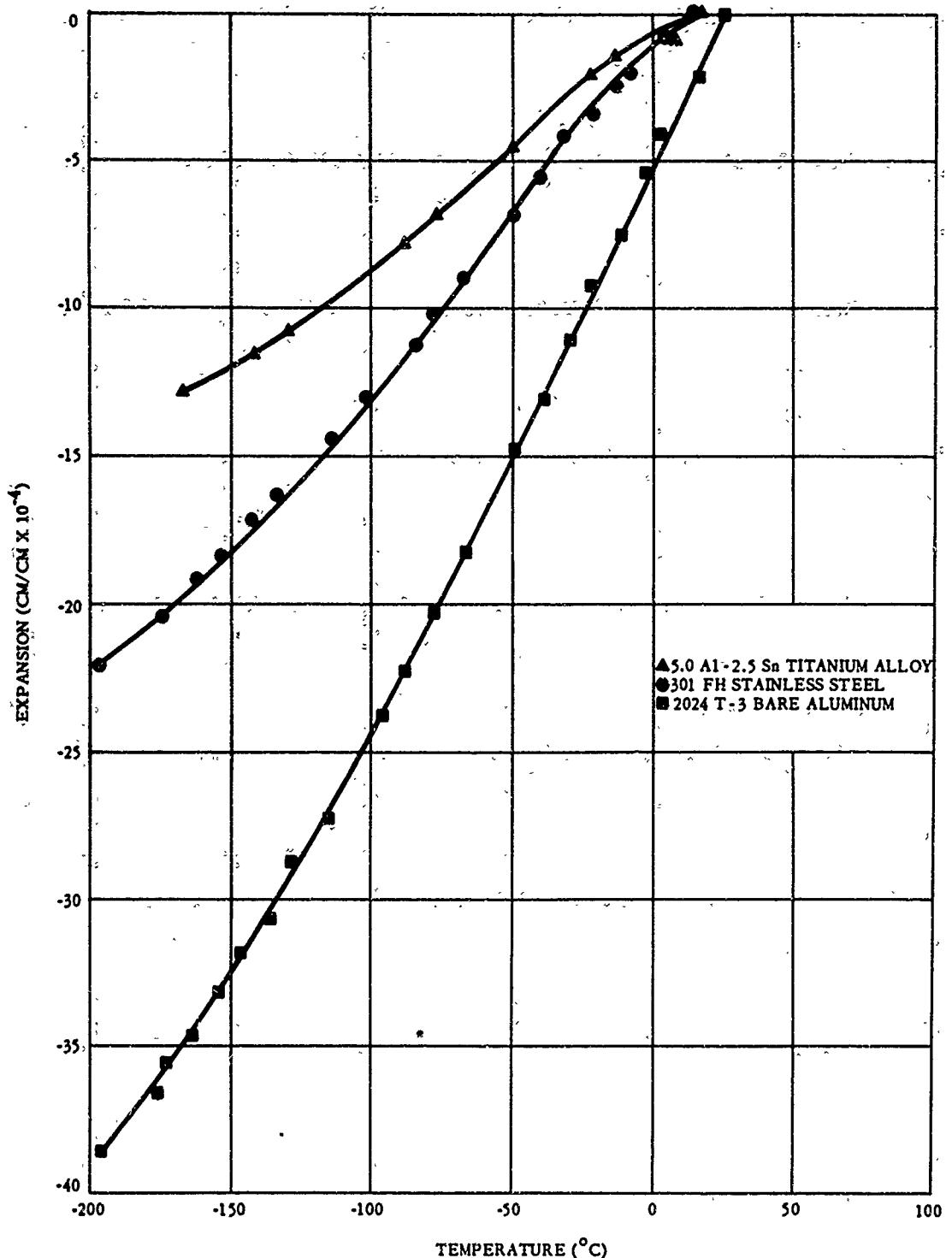


Figure 14. Total linear thermal expansion of some adherends.

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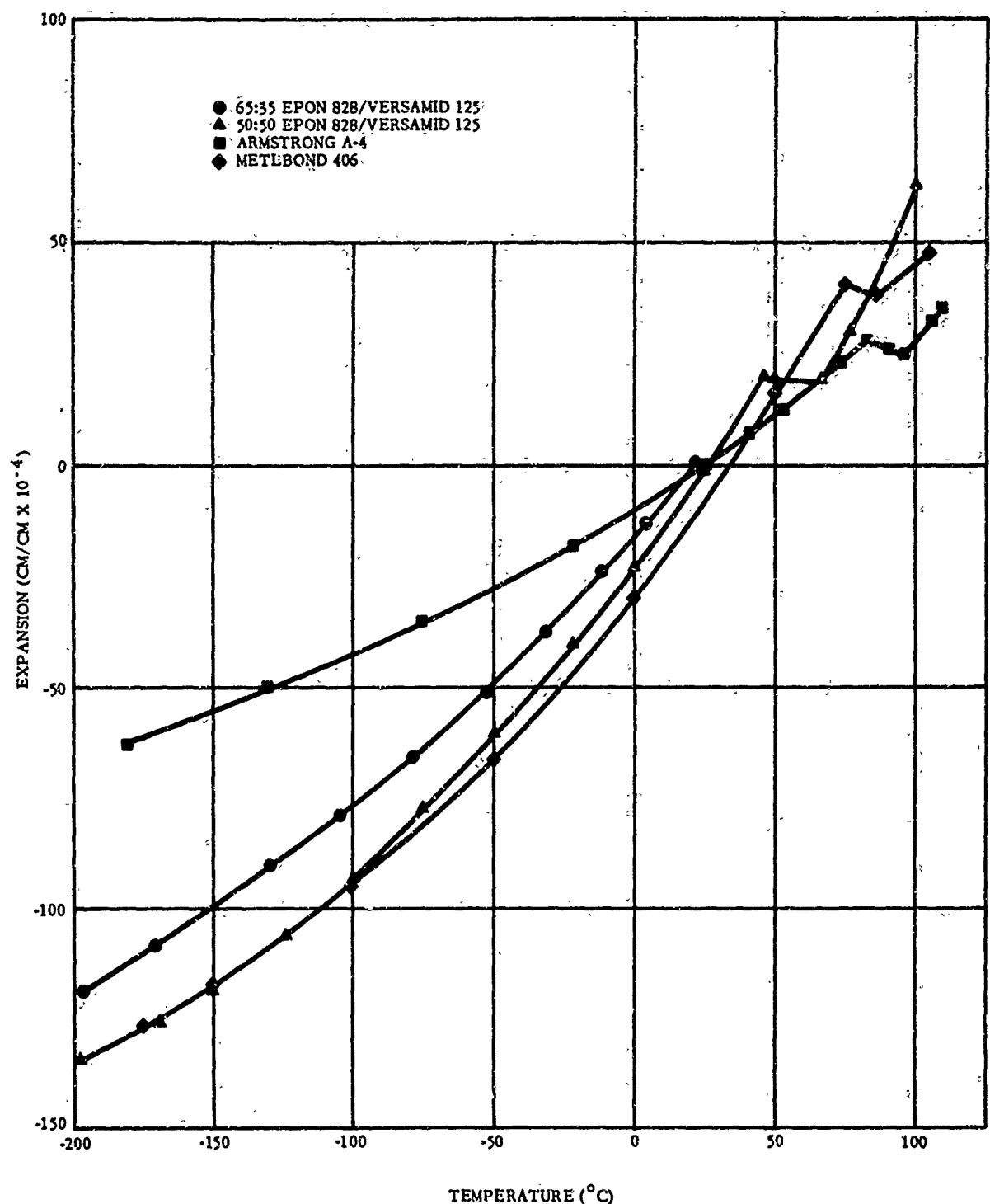


Figure 15. Total linear thermal expansion of some adhesive systems.

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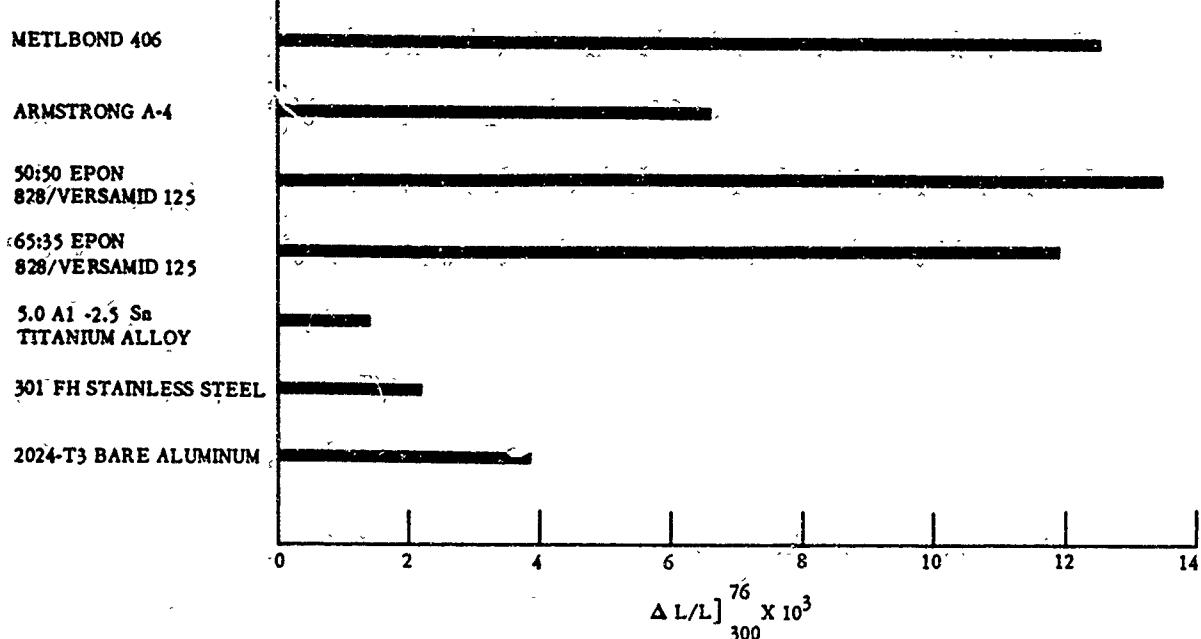


Figure 16. Total linear thermal expansion of adhesives and adherends tested at Astronautics.

Pi-tension testing of sandwich structures having both stainless steel and titanium faces bonded to 5.7-pcf fiberglass honeycomb core has been conducted over the temperature range of -423° to 78°F (see Figures 21 and 22). In most cases, failure occurred primarily in the core. The best adhesives for bonding sandwich structures for use at cryogenic temperatures have proved to be the epoxy-nylon unsupported tapes and the filled epoxy-phenolic supported tapes. The pi-tension tests have shown that the -320°F strengths are much higher than those obtained at 78°F. The -423°F pi-tension results are somewhat lower than those obtained at -320°F, but are still considerably higher than the room-temperature strengths; therefore, room-temperature tension allowables on the honeycomb core can be safely used when subjecting the core to cryogenic environments.

Plate shear testing of sandwich panels have also been tested from -423° to 78°F (see Figure 23). Again, an increase in strength was noted when going from 78° to -320°F; however, average strength at -423°F was lower than the room-temperature strength. This may be a result of the small number of specimens tested. It appears that there is a need for additional evaluation in this area.

GENERAL DYNAMICS | ASTRONAUTICS

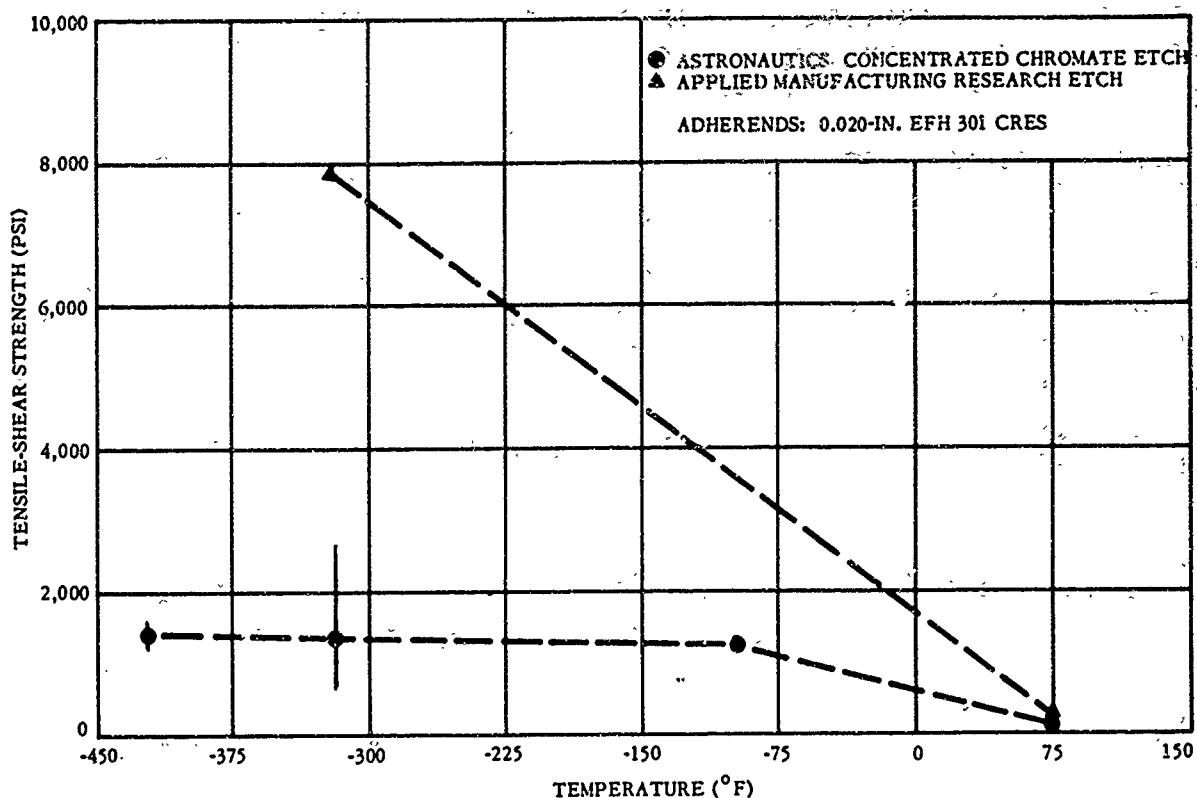


Figure 17. Tensile-shear strength of Coast Pro-Seal 777 vs. temperature.

Fatigue tests were run on pi-tension specimens having 0.032-in. EFH 301 stainless steel faces, Hexcel HRP-3/16 core (5.5 pcf) and epoxy-nylon adhesives. Specimens were fatigued at  $-423^{\circ}\text{F}$ , at a rate of 5 to 10 cps from 0 to 600 psi. As many as 23,000 cycles were run on one specimen without failure. This specimen was then slowly brought to a stress level of 900 psi before it failed.

One purpose of this REA was to attempt to correlate the adhesive strengths at cryogenic temperatures with some basic physical properties of the resin system or the basic molecular structure of the resin. As stated previously, thermal expansion data failed to reveal any correlation between bond strength and resin system. Work accomplished at Narmco (Ref. 12) has also led to this conclusion. In fact, when investigating the thermal expansion data of two epoxy-nylon systems, it was found that the system containing the most nylon showed less contraction than the system containing an appreciably lower amount of nylon. This occurred even though nylon has a much higher coefficient of expansion than the particular epoxy resin used in the adhesives. However,

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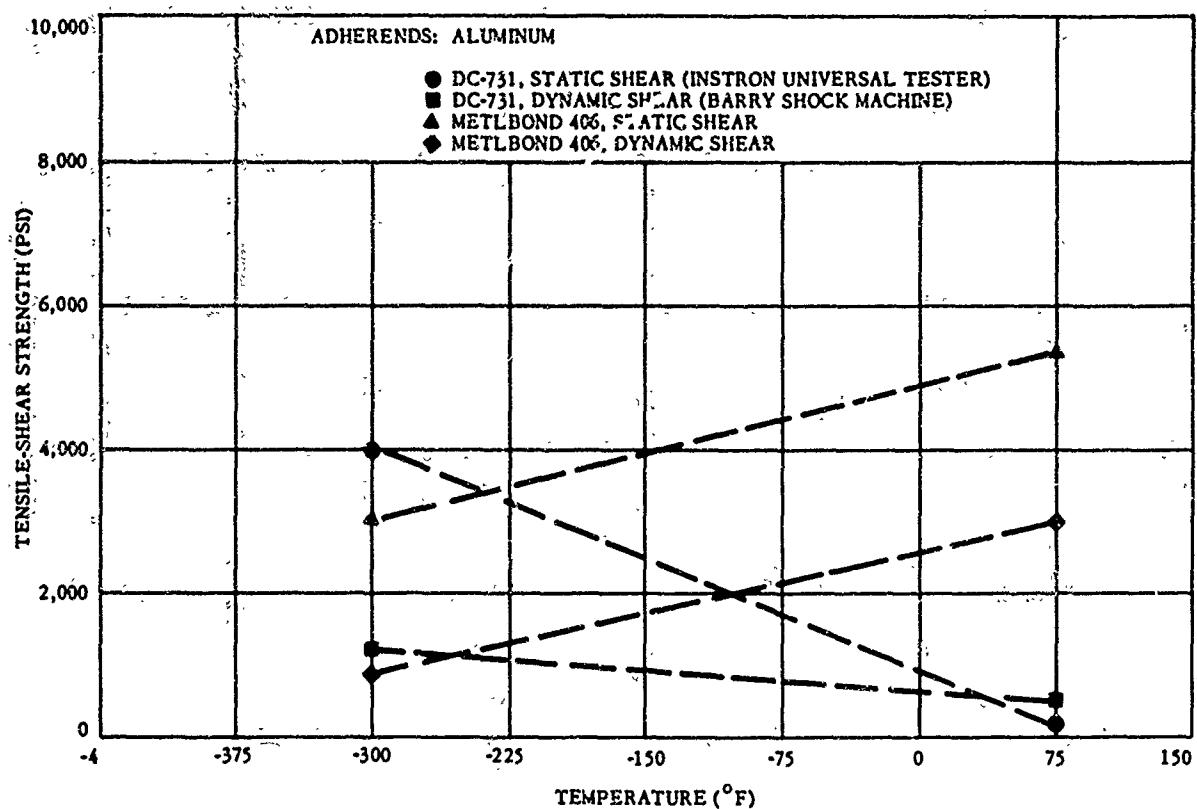


Figure 18. Static and dynamic tensile-shear strengths of adhesives tested at Hughes Aircraft Co.

other factors such as degree of crosslinking, degree of cure, method of adhesive processing, crystallinity, etc., can influence the thermal expansion of adhesive systems.

One of the problems with attempting to correlate adhesive strength with molecular structure is that adhesive systems in most cases are proprietary. Another difficulty is that the raw materials used in the adhesives, as well as the compounded adhesives themselves, vary from batch to batch. Degree of cure, length of storage prior to bonding, method of manufacture, and many other factors affect the strength of the bond. Therefore, it is possible to start with the same basic components and find that the final properties of the adhesives vary considerably, particularly at temperature extremes. It is not unusual to find a large variance in bond strength of an adhesive from batch to batch.

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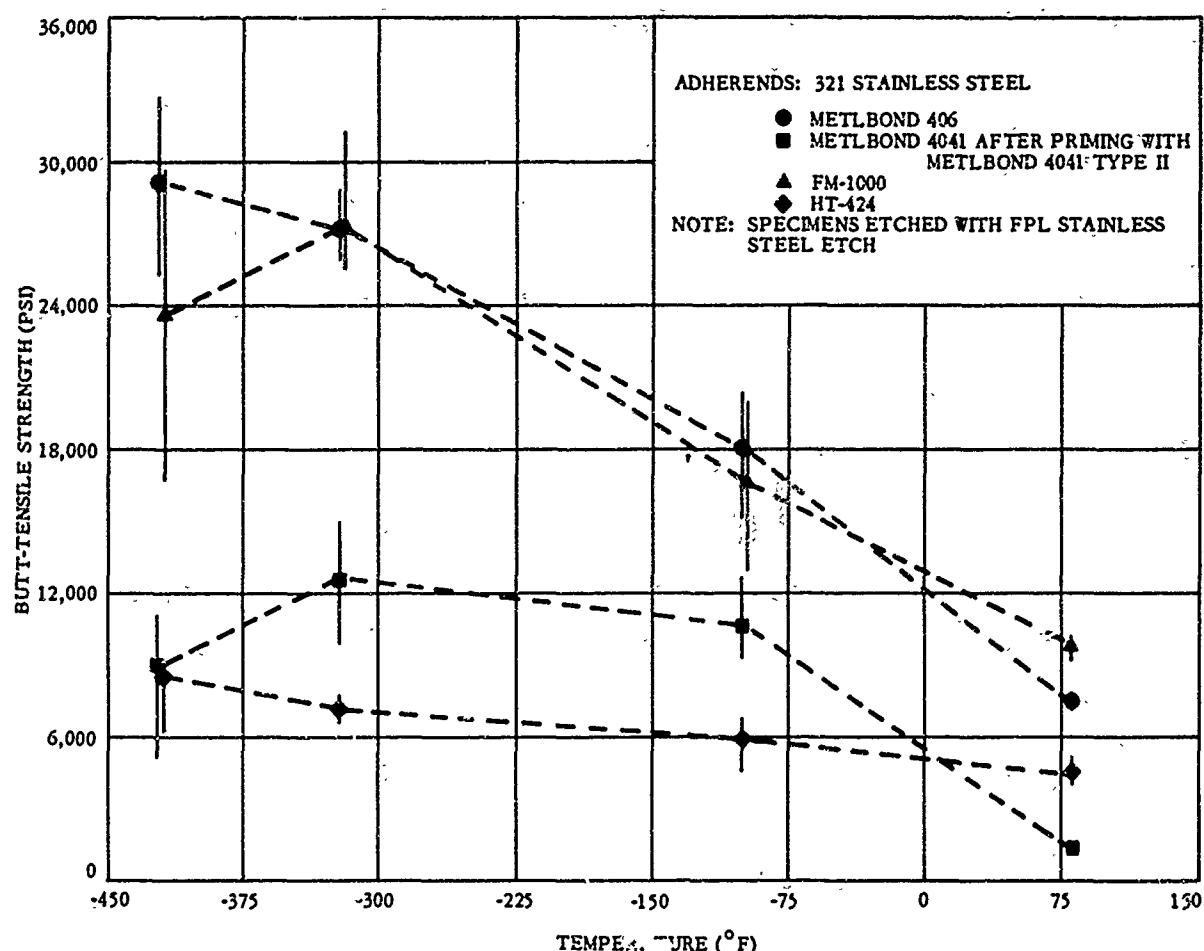


Figure 19. Butt-tensile strength of various adhesives vs. temperature.

GENERAL DYNAMICS | ASTRONAUTICS

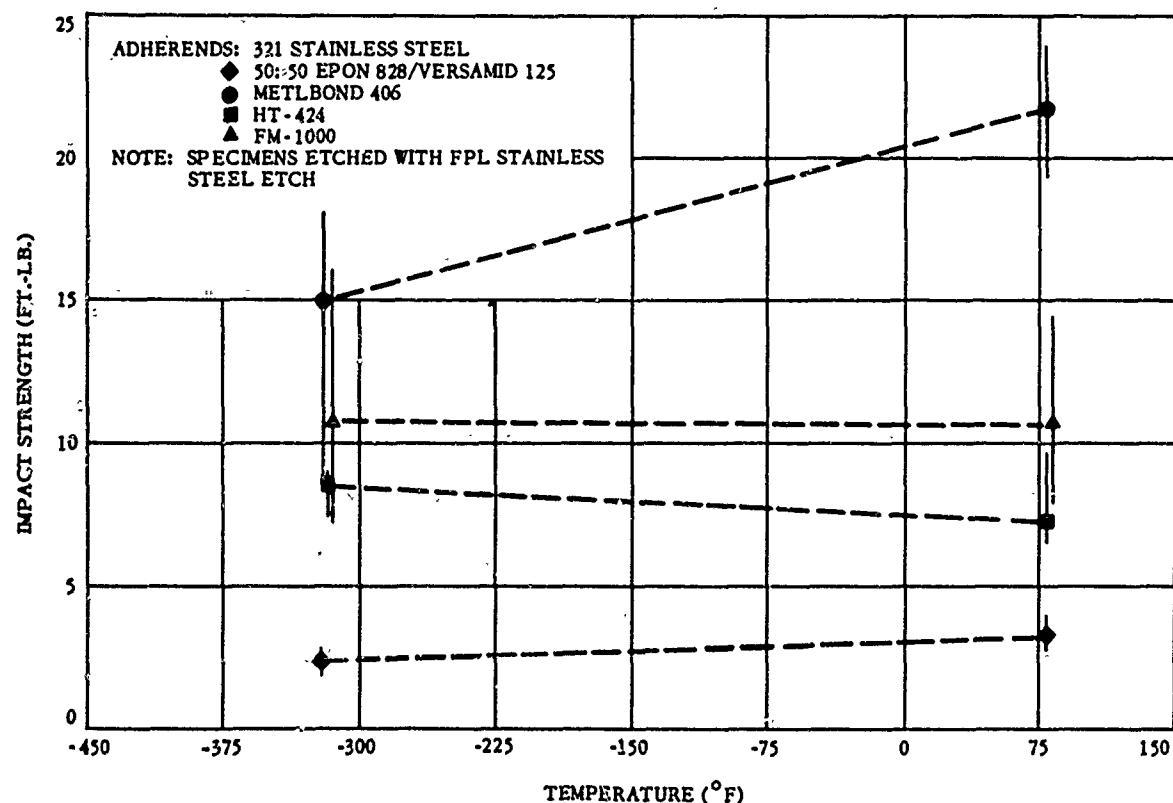


Figure 20. Impact strength of various adhesives vs. temperature.

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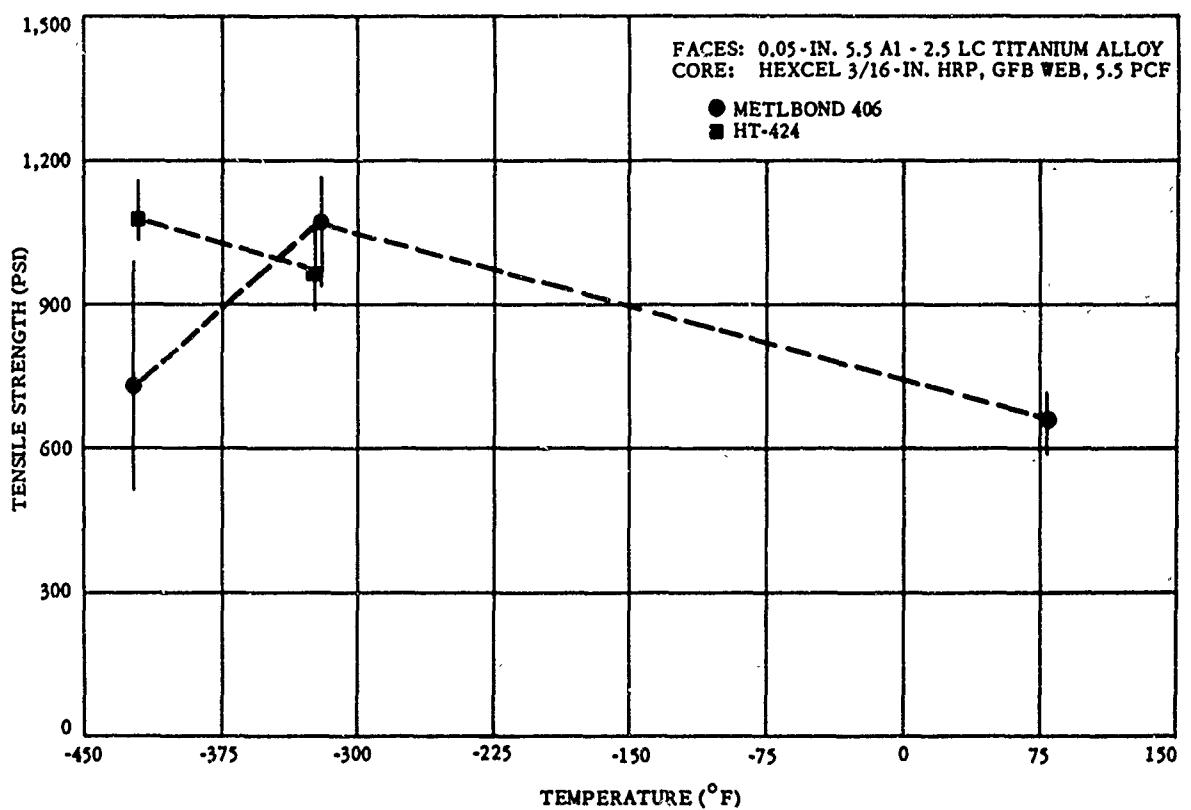


Figure 21. Pi-tension tests of sandwich panels having titanium faces and fiberglass core.

GENERAL DYNAMICS | ASTRONAUTICS

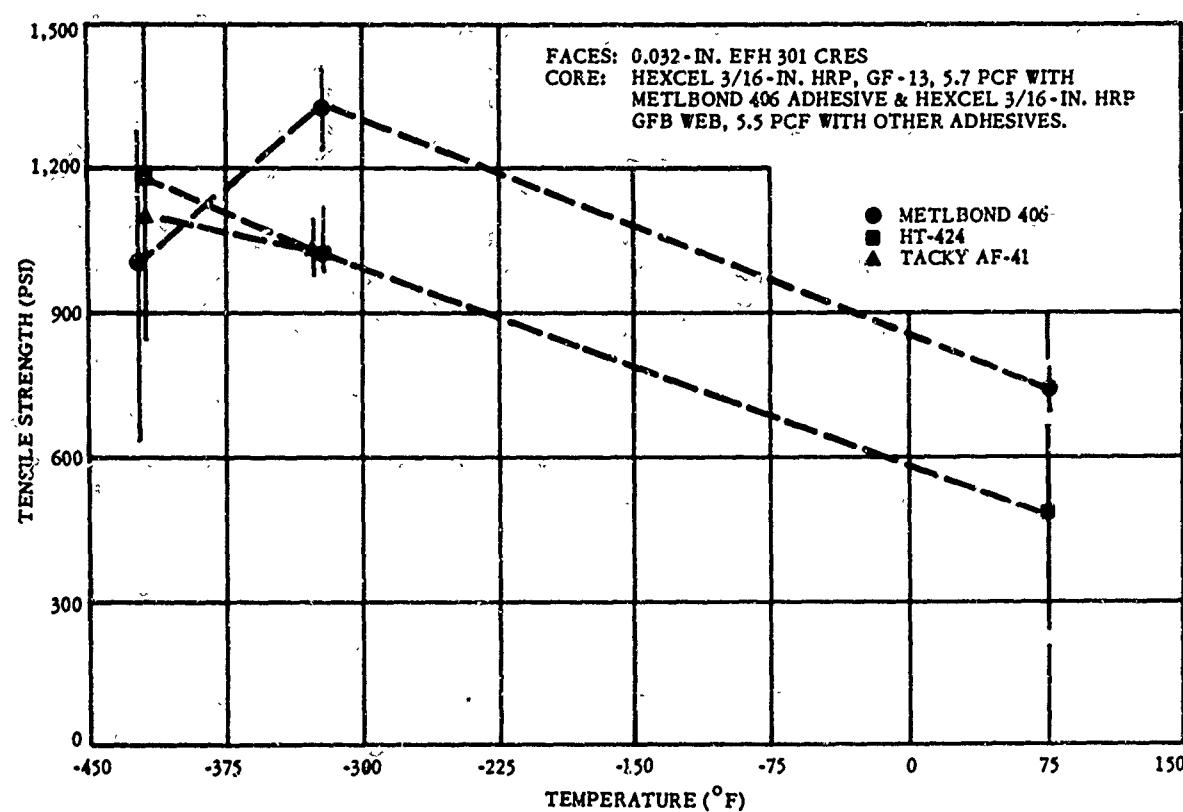


Figure 22. Pi-tension tests of sandwich panels having stainless steel faces and fiberglass core.

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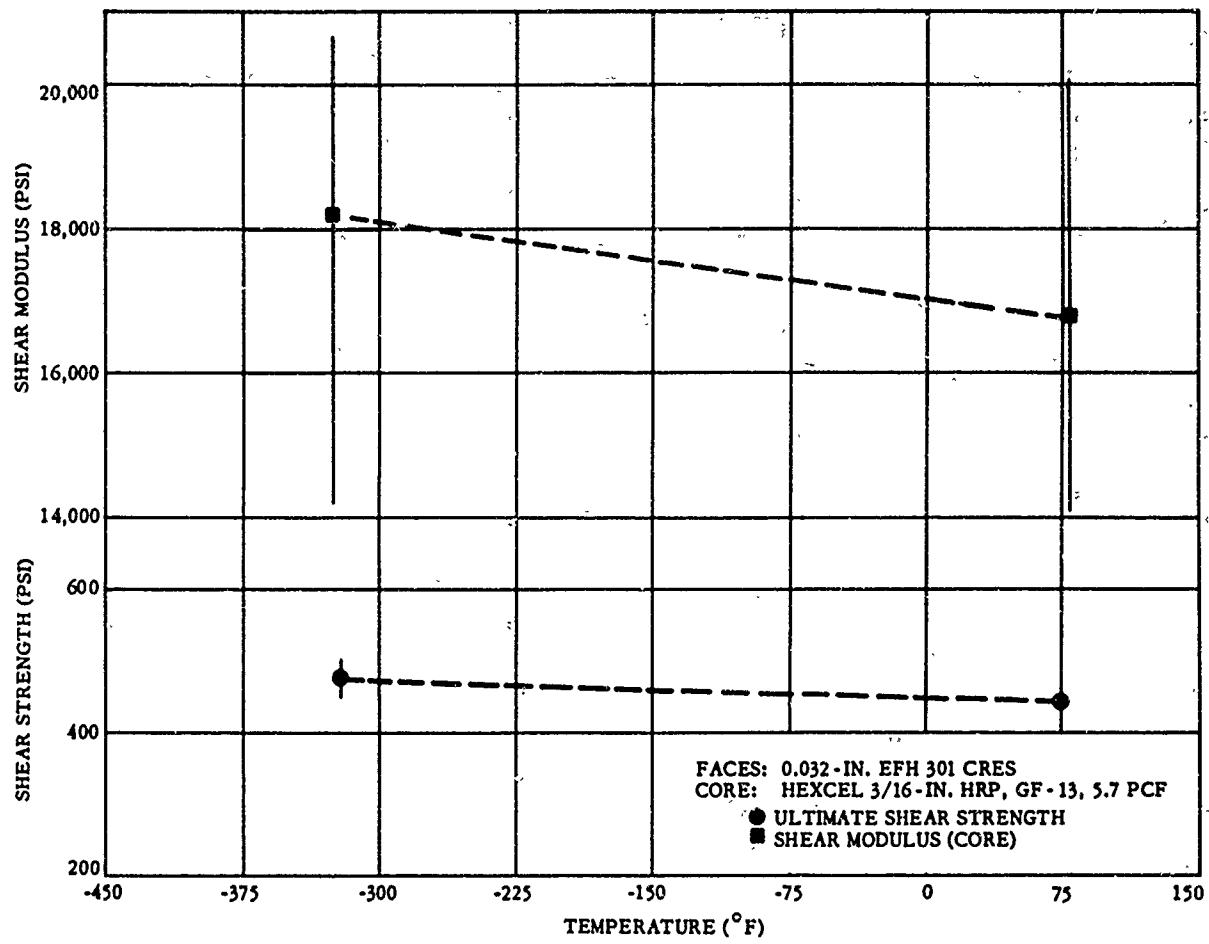
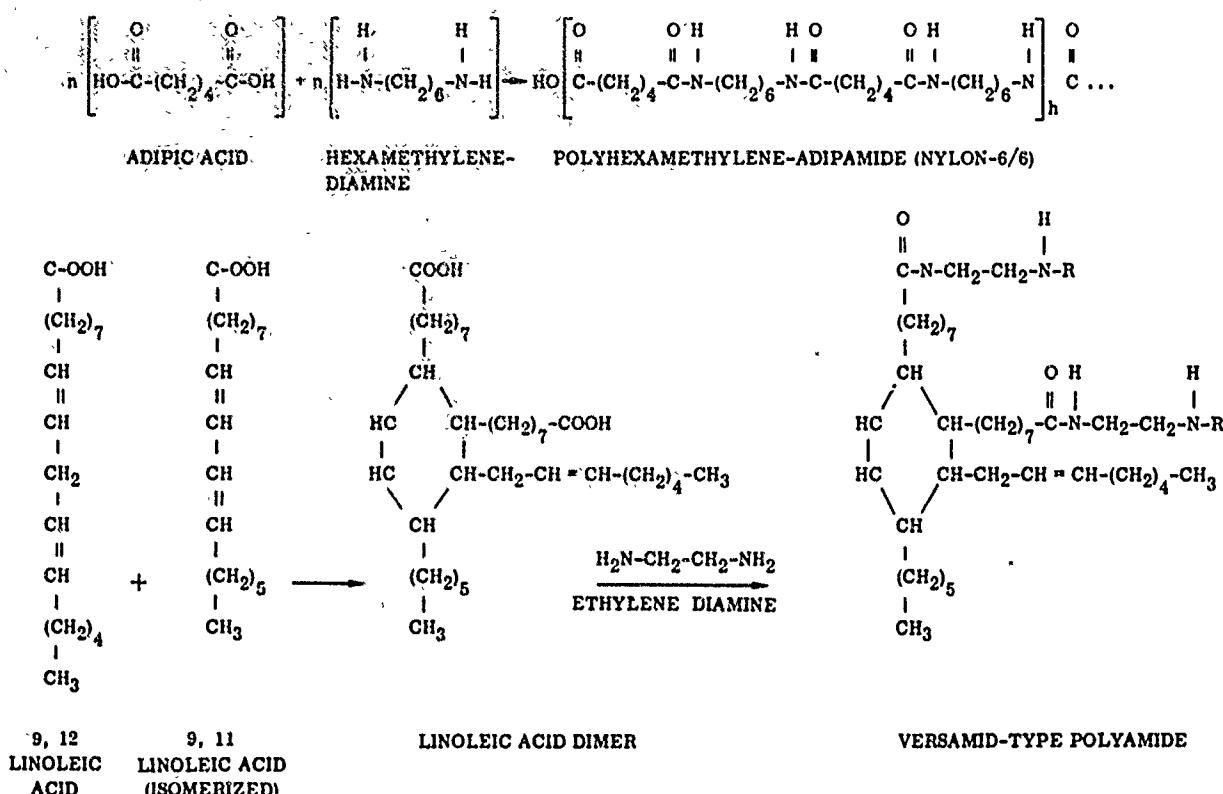


Figure 23. Shear properties of honeycomb panels bonded with Metlbond 406.

GENERAL DYNAMICS | ASTRONAUTICS

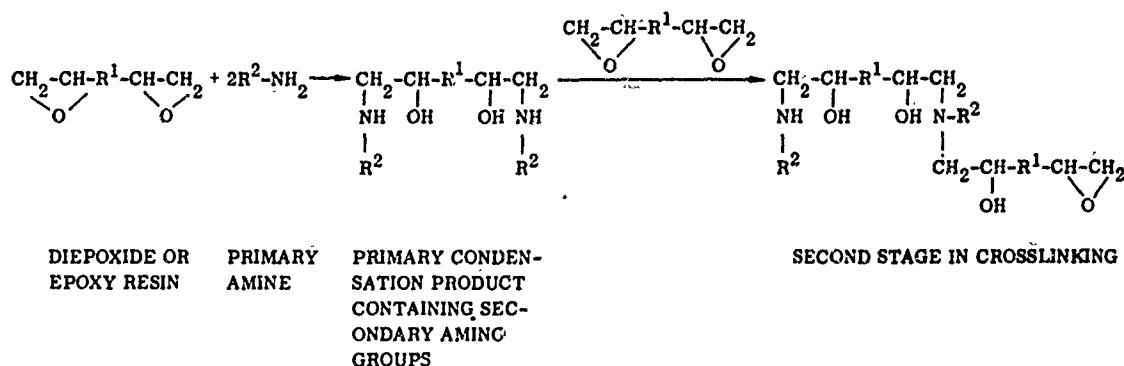
Infrared curves were run on the adhesives evaluated in this program (see Figures 24 through 34). Of prime interest were the four epoxy-nylon unsupported tapes (Metl-bond 406, AF-40, AF-41, and FM-1000), and the two epoxy-polyamide systems (Narmco 3135 and Resiweld No. 4). The generic name nylon refers to a member of the polyamide family and is defined by the DuPont Co. as follows: "A generic term for any long-chain synthetic polymeric amide which has recurring amide groups as an integral part of the main polymeric chain and which is capable of being formed into a filament in which the structural elements are oriented in the direction of the axis."

The nylon materials commercially available are made by self-condensation of amino acids or the reaction of dibasic acids with diamines. Those most commonly used are: polyhexamethylene-adipamide (nylon-6/6), polyhexamethylene-sebacimide (nylon-8/10), n-alkoxy methyl substituted polyhexamethylene-adipamide (nylon-8), polycaprolactum (nylon-6), and polyamide from 11-aminodecanoic acid (nylon-11). Another polyamide commonly used is the "Versamid" type which is made by the condensation of dimerized vegetable oil acids and suitable polyamino compounds. The Versamid type is the one commonly used in the room-temperature curing epoxy-polyamides (Narmco 3135, Resiweld No. 4, etc.). The condensation reactions for the formation of the nylon-6/6 and the Versamid type polyamides are as follows (where R may be hydrogen or another linoleic acid dimer group, Ref. 13):

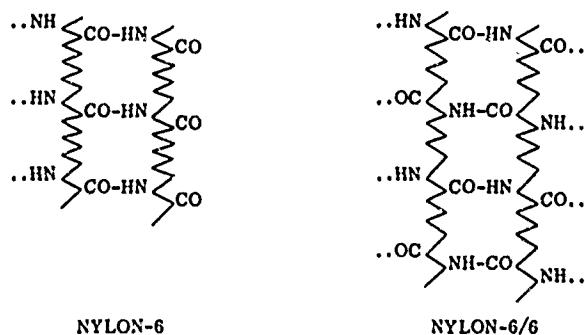


GENERAL DYNAMICS | ASTRONAUTICS

When amines having higher functionality than ethylene diamine are used, the resinous product will have active amine hydrogens (rather than amide hydrogens) capable of reacting with epoxy resins just as ordinary polyamines. Because of the bulk of this polymer, the Versamid-type polyamide would not be expected to result in hydrogen bonding (steric hindrance effect), and in most cases would result in an amine-type reaction with an epoxy.



In contrast to the preceding type of reaction, the nylon-6/6, nylon-6, etc., are very linear and are capable of aligning themselves so that hydrogen bonding is prevalent:



The hydrogen bond is a weaker crosslinking bond; it has a dissociation energy of about 2 to 5 Kcals/mole, compared to about 50 Kcals/mole for a C-C bond. The incorporation of a sufficient number of hydrogen bonds as crosslinkages results in desirable properties at room temperature and imparts to the adhesive the necessary strength at very low temperatures without the penalty of brittleness produced by covalent linkages. In the case of the unsupported epoxy-nylon tapes, enough catalyst is generally added to fully polymerize the epoxy. The epoxy can actually be considered

## GENERAL DYNAMICS ASTRONAUTICS

to act as a reactive diluent in contrast to the reaction with the Versamid-type polyamide. This results in the epoxy-polyamide (Versamid type) being more brittle than the epoxy-nylon unsupported tapes. It also accounts for the toughness of the epoxy-nylon unsupported tapes at cryogenic temperatures.

Examination of the infrared curves of the epoxy-nylon unsupported tapes revealed that they had almost identical spectra. There was no attempt to obtain relative percentages of individual groupings because at the time there was no means available of accurately controlling the specimen thickness. The Metbond 406 and AF-41 appear to use dicyandiamide as a catalyst since only in these two systems did the cyano grouping at 4.5 to 4.6 microns appear. It is believed that FM-1000 uses diamino diphenyl sulfone as a catalyst since the sulfone grouping at 8.7 microns is apparent in its spectrum. The catalyst used in the AF-40 was not readily apparent. Because of the limited amount of information on the exact composition of the epoxy-nylon unsupported tapes there can be no definite conclusions drawn as to the effect of catalyst type on the cryogenic properties.

The infrared curves on Narmco 3135A and Resiweld No. 4 (Component A), are almost identical to the published curve on Epon 828, while the spectra on Narmco 3135B and Resiweld No. 4 (Component B) are almost identical to the published spectra on Versamid 125.

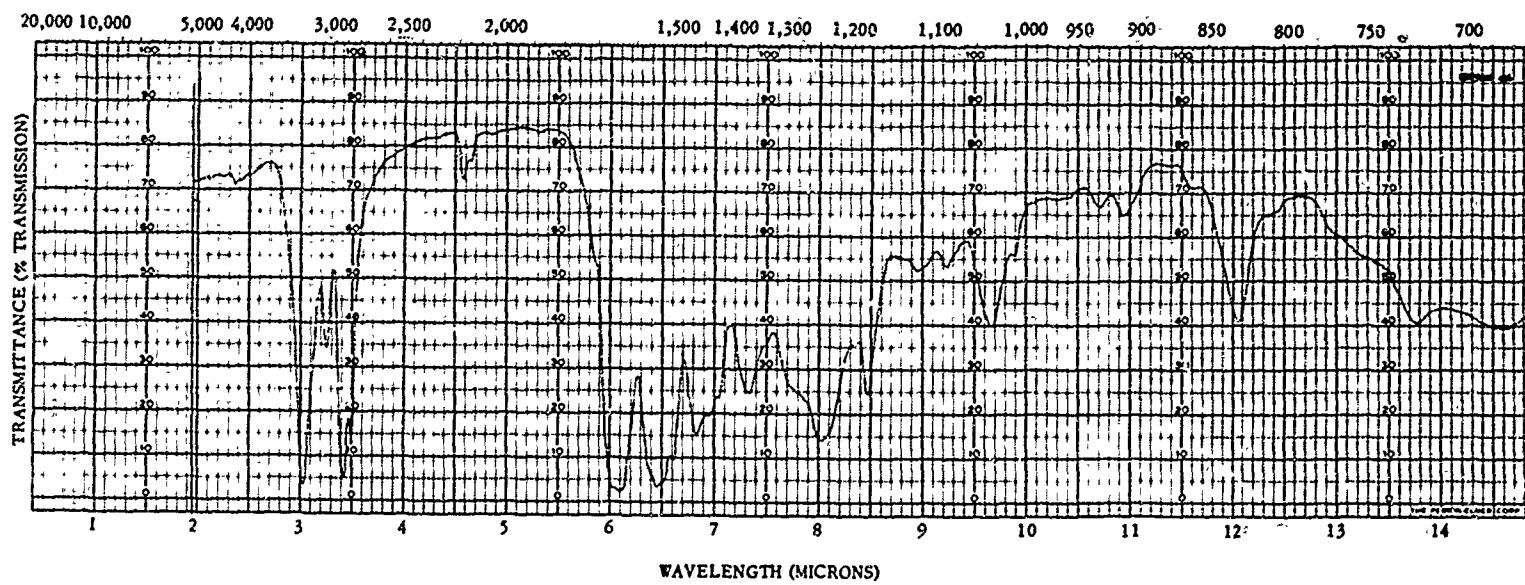


Figure 24. Spectrum of Metlbond 406.

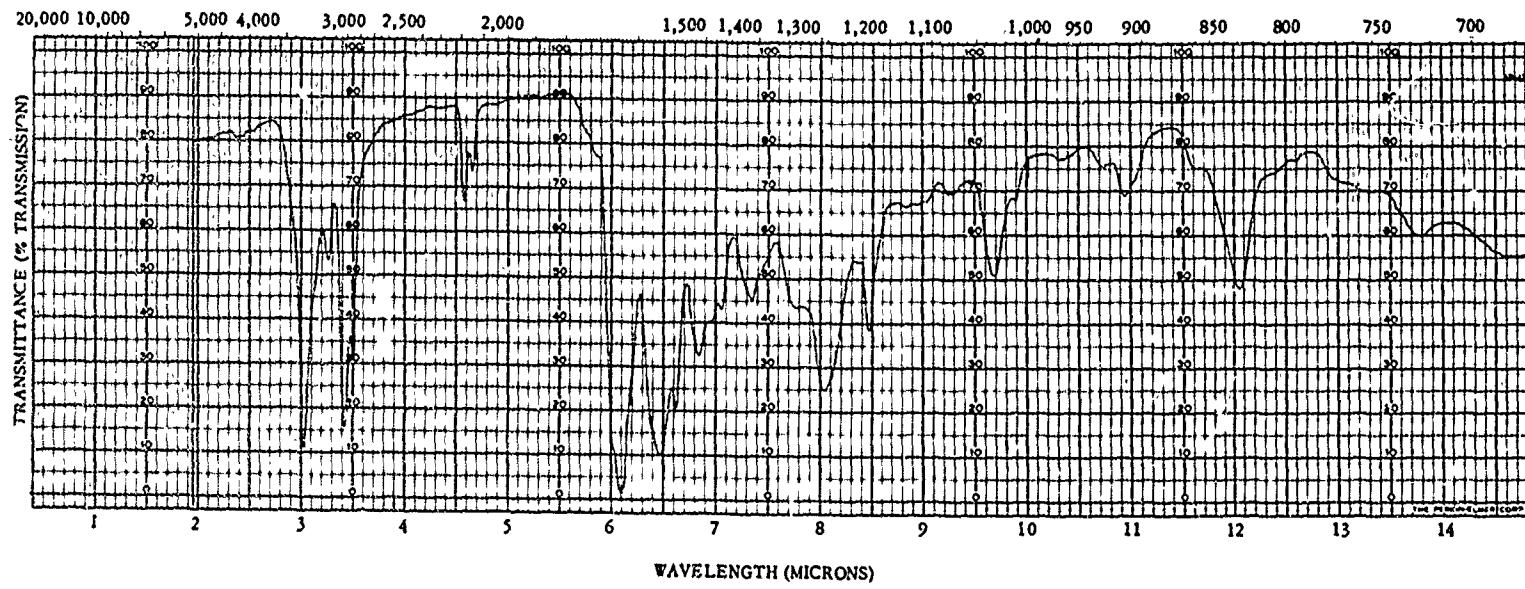
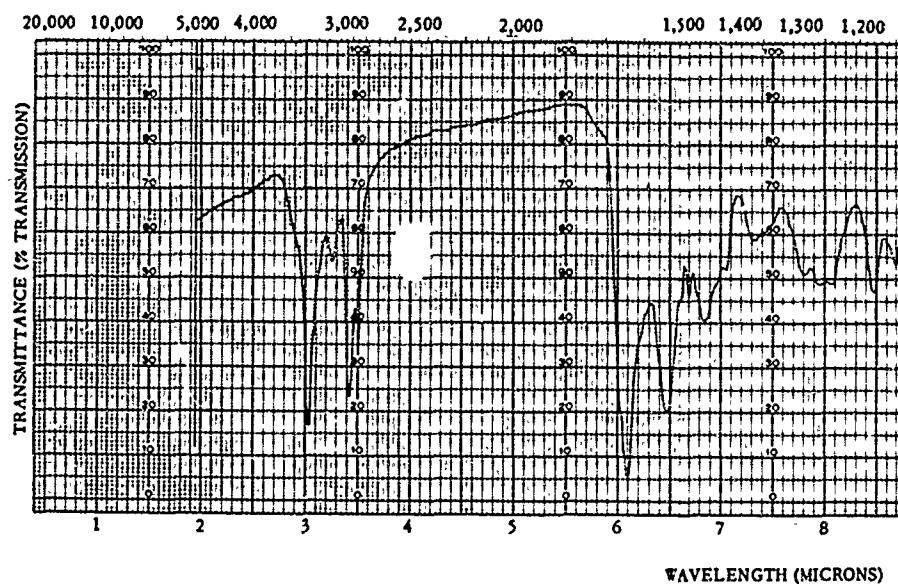
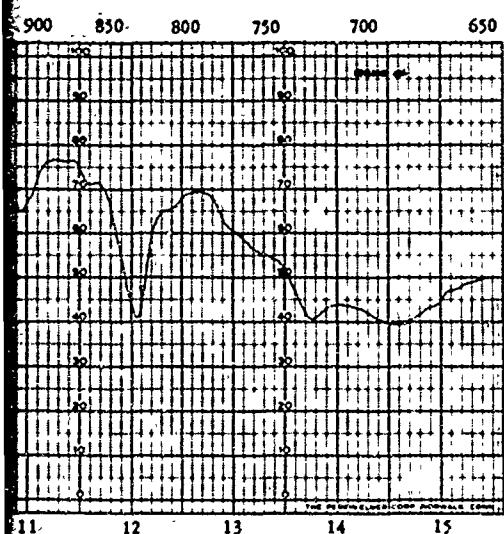


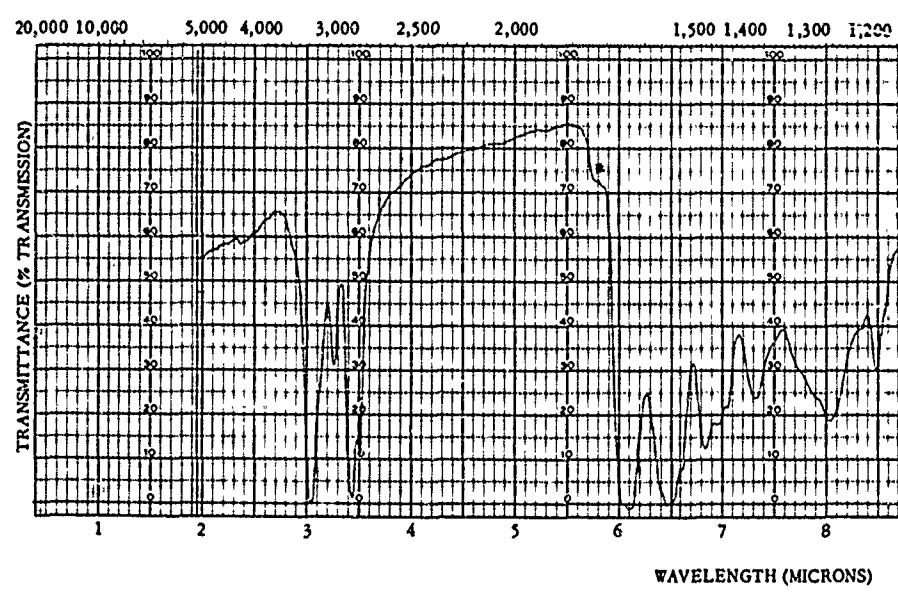
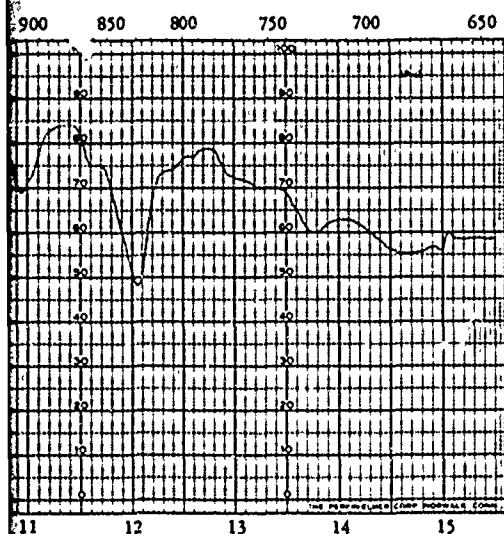
Figure 25. Spectrum of AF-41.

A.



WAVELENGTH (MICRONS)

Figure 26. Spectrum



WAVELENGTH (MICRONS)

Figure 27. Spectrum

B.

GENERAL DYNAMICS | ASTRONAUTICS

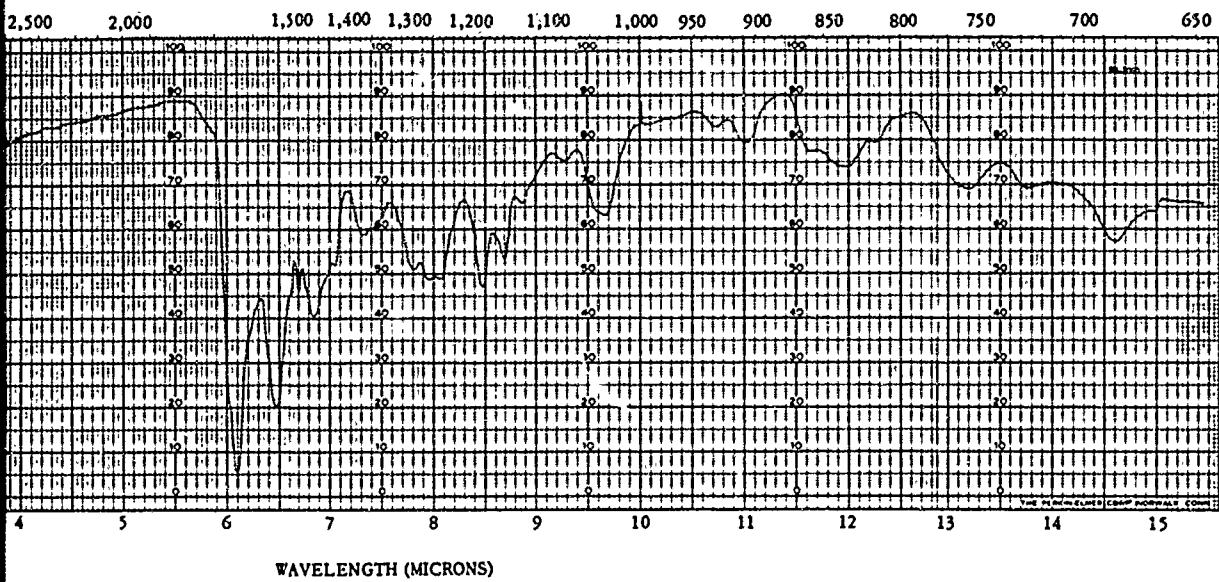


Figure 26. Spectrum of FM-1000.

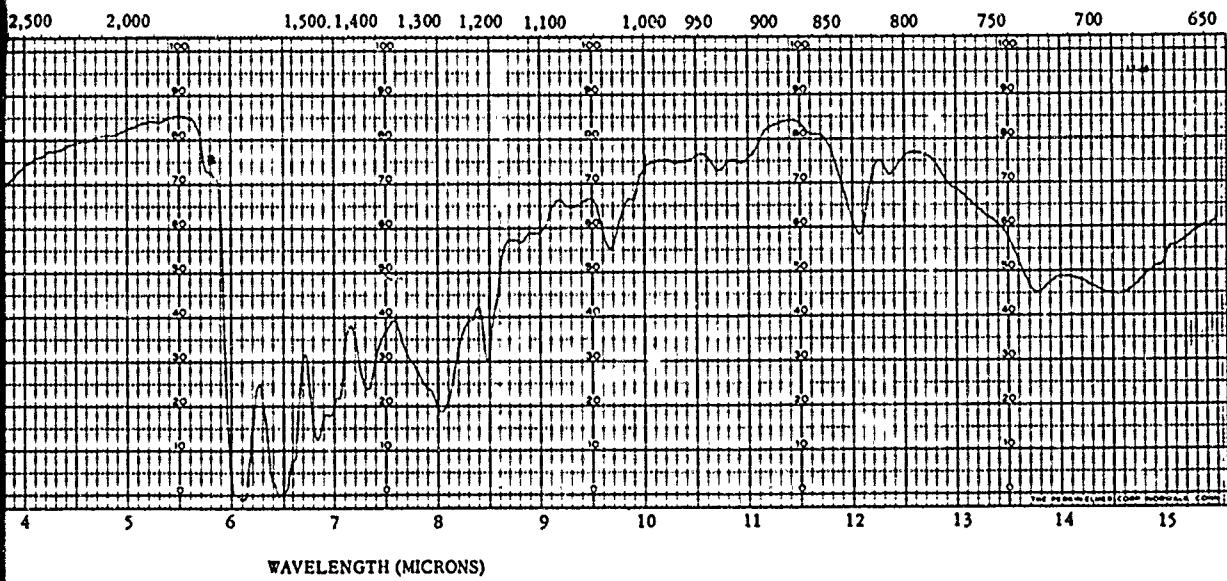


Figure 27. Spectrum of AF-40.

GENERAL DYNAMICS | ASTRONAUTICS

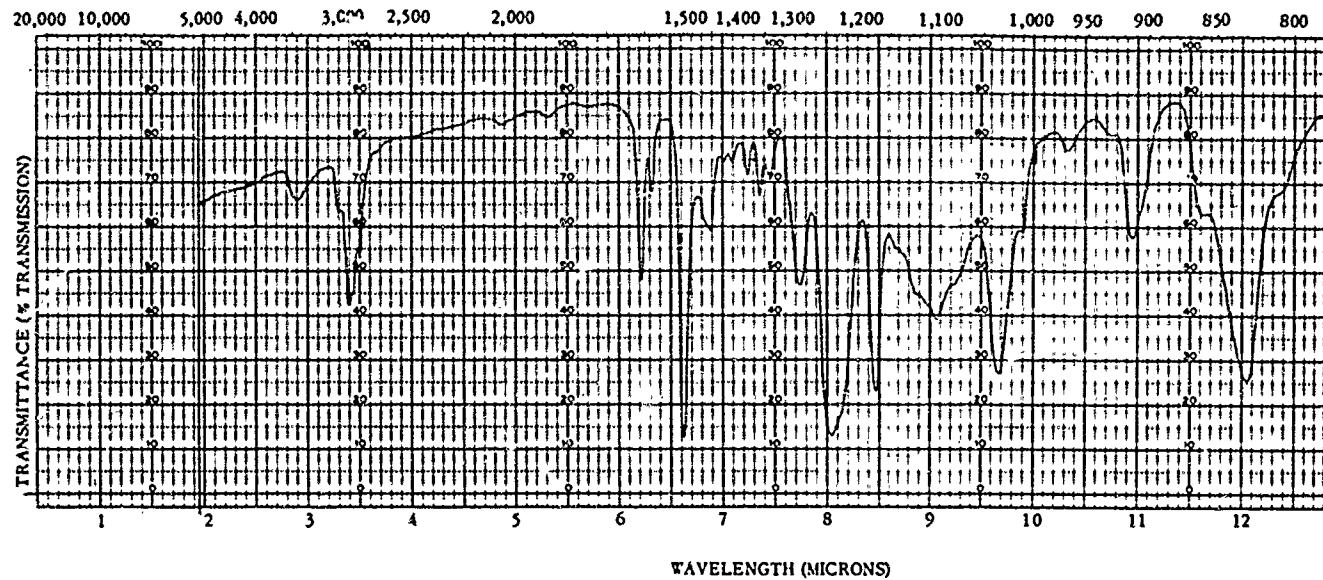


Figure 28. Spectrum of Resiweld No. 4, Component A.

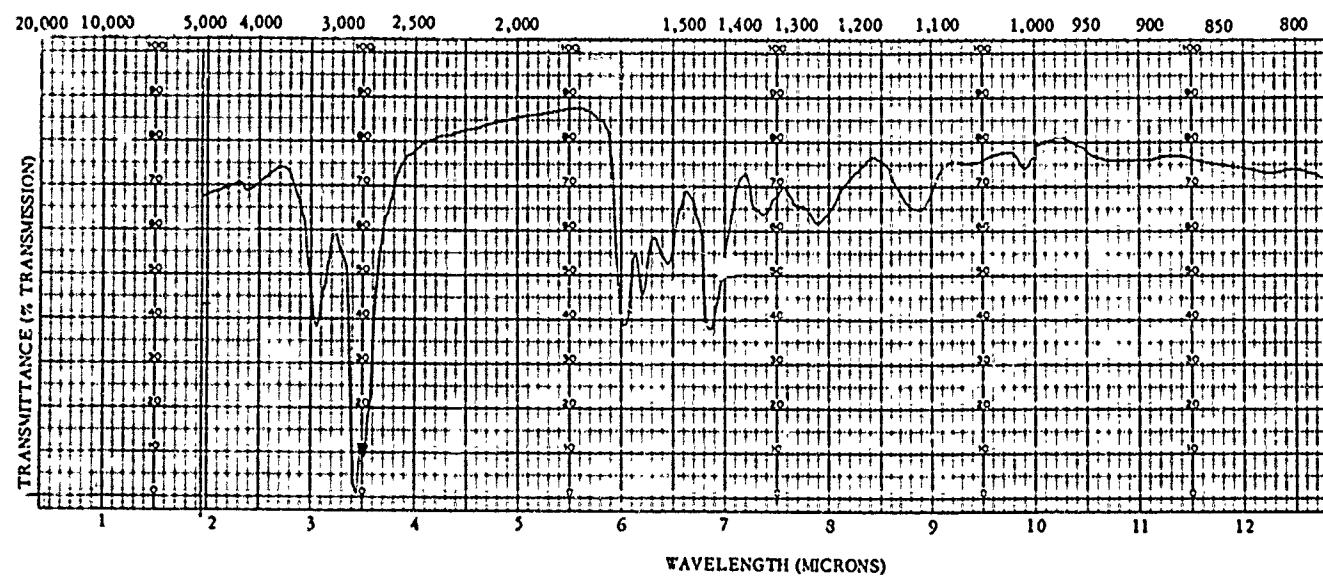


Figure 29. Spectrum of Resiweld No. 4, Component B.

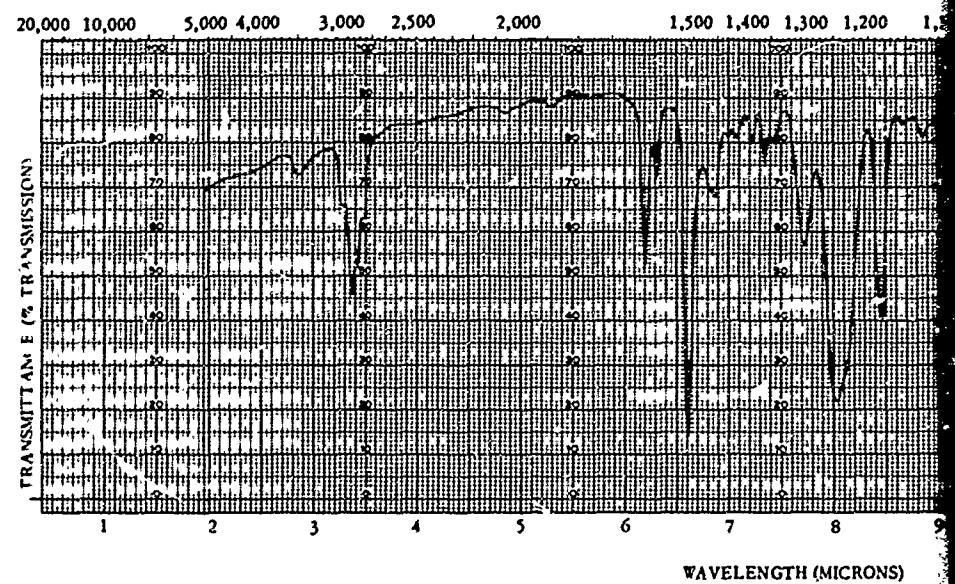
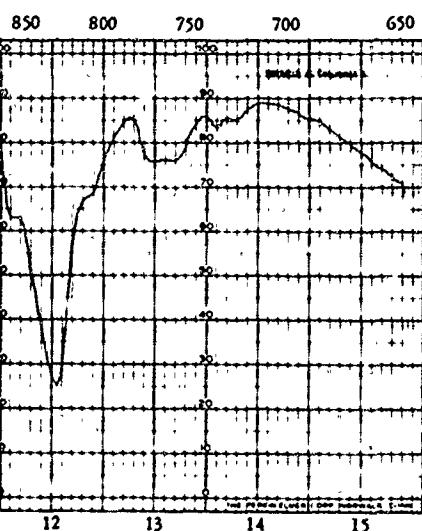


Figure 30. Spectrum of Narmco 3135,

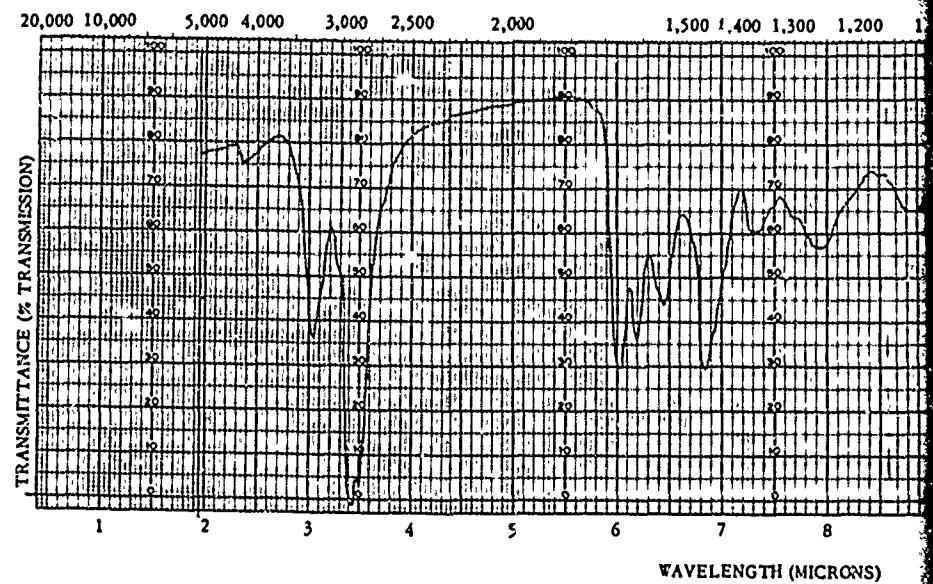


Figure 31. Spectrum of Narmco 3135,

B.

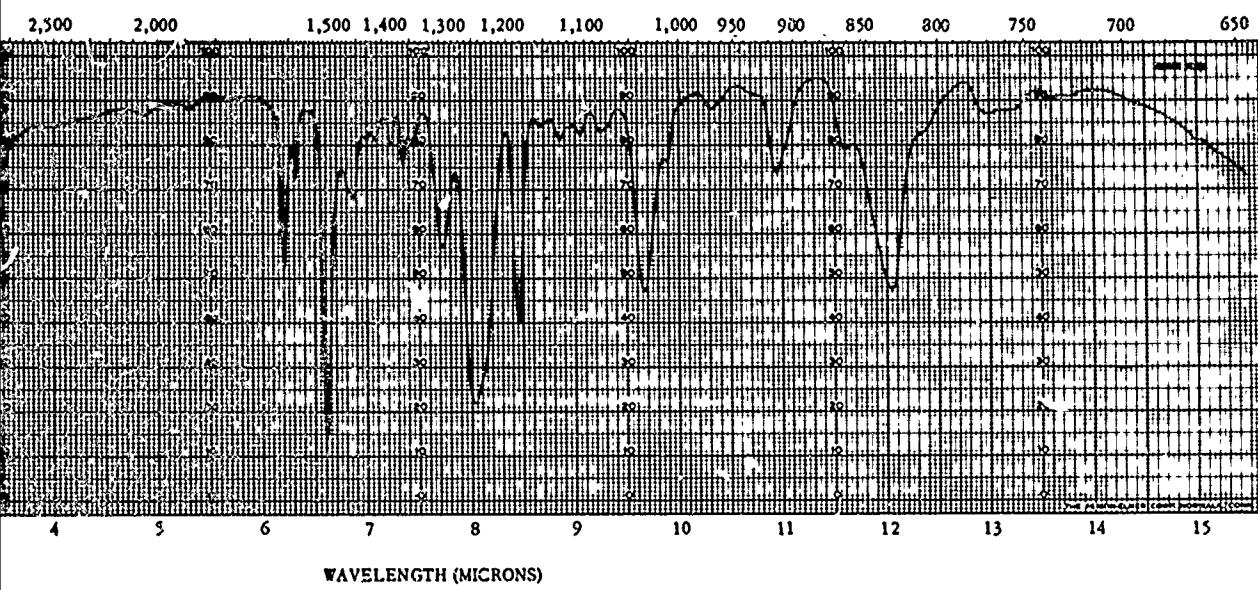


Figure 30. Spectrum of Narmco 3135, Component A.

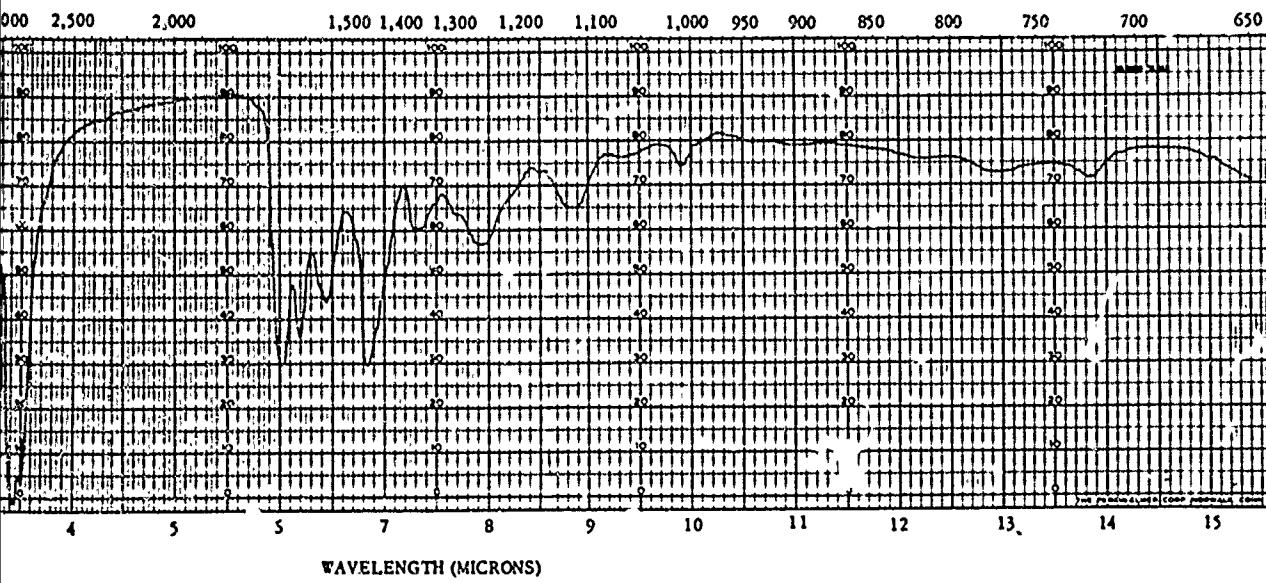


Figure 31. Spectrum of Narmco 3135, Component B.

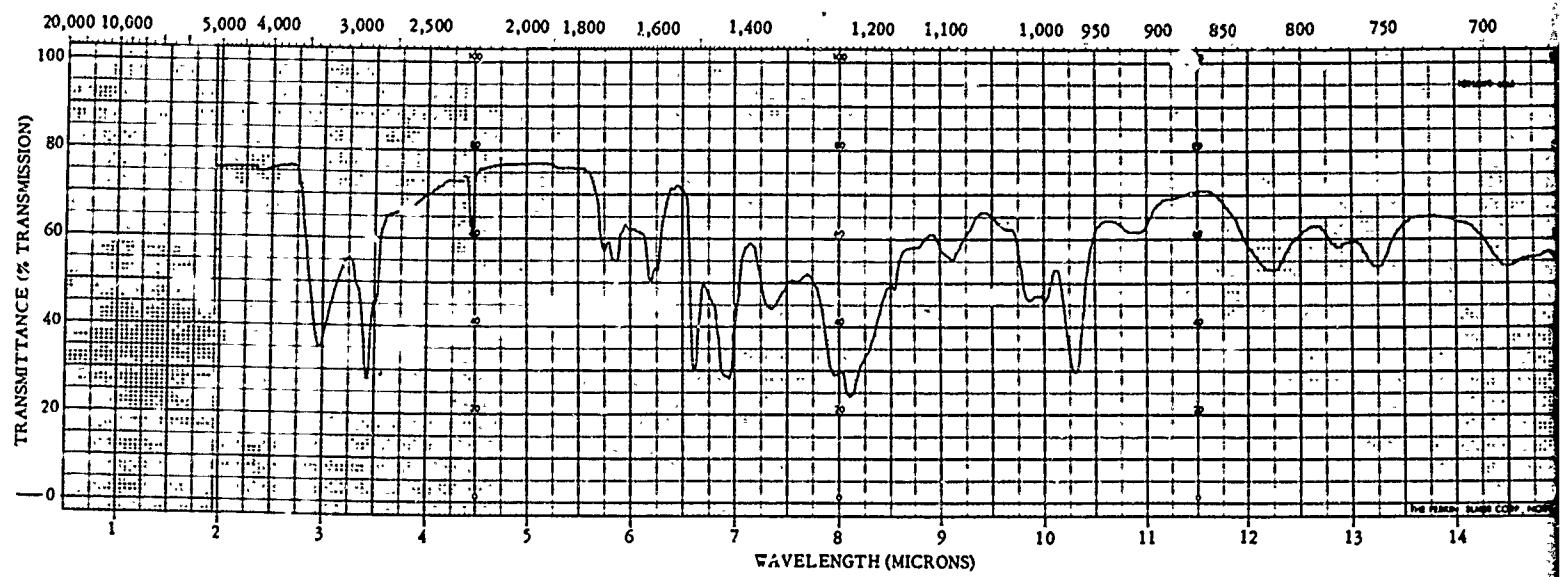


Figure 32. Spectrum of Metlbond 4041.

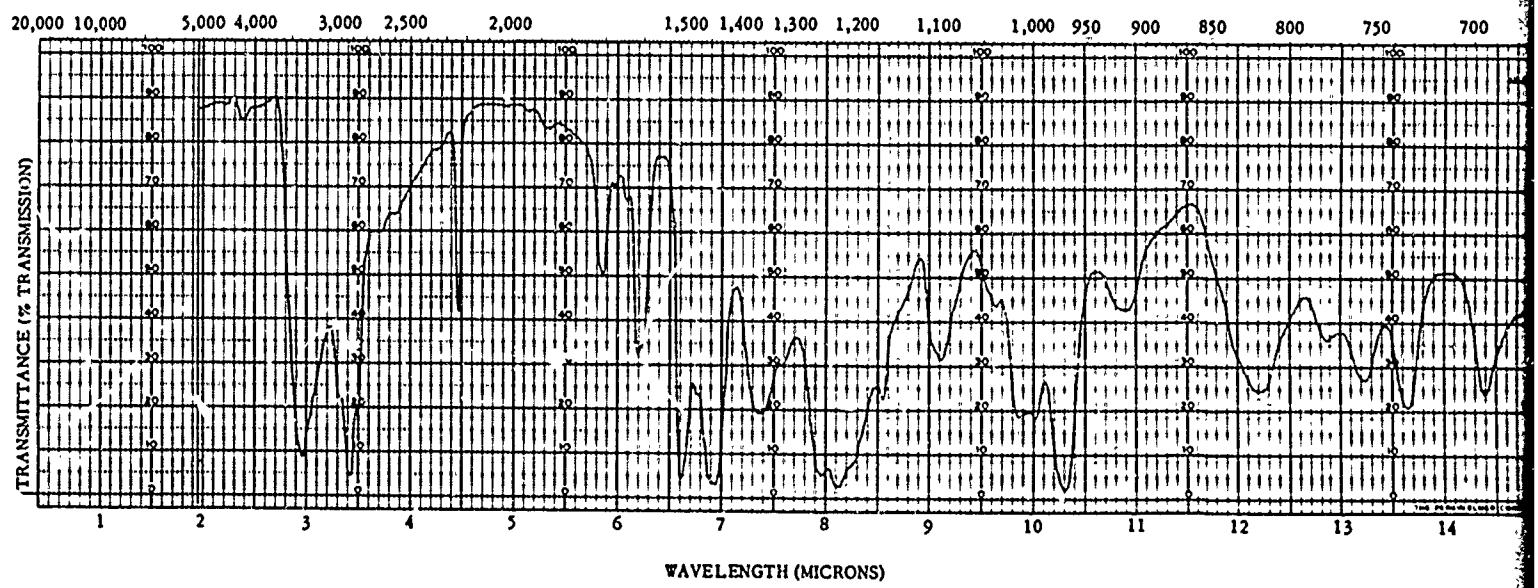
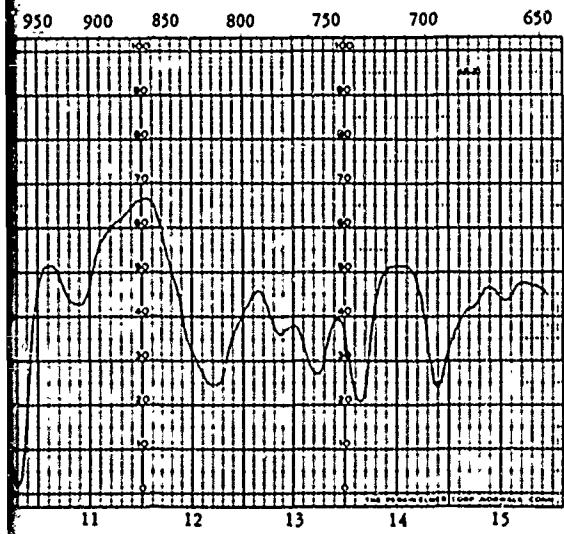
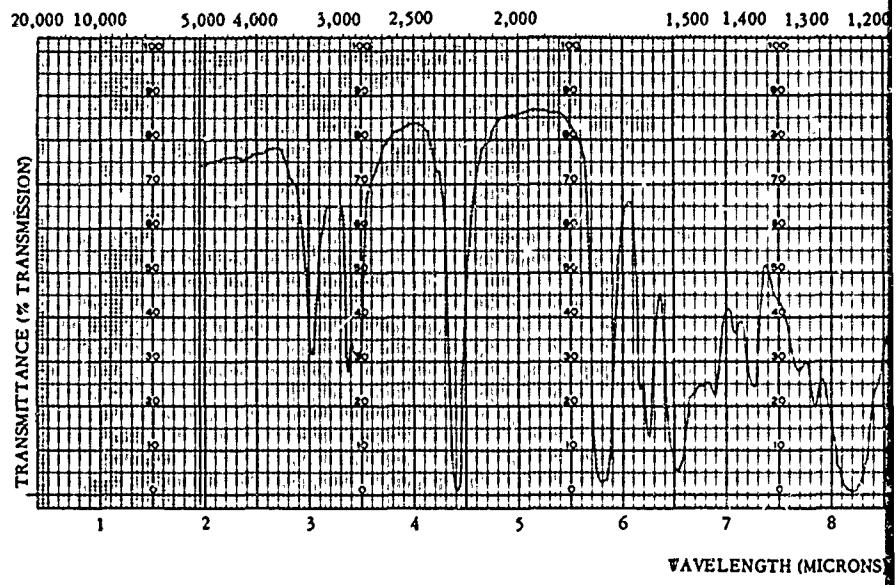
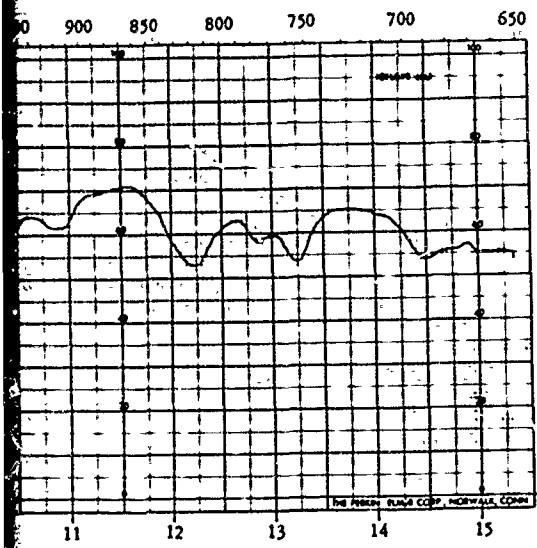


Figure 33. Spectrum of AF-32.

A.



B.

Figure 34. Spectrum o

GENERAL DYNAMICS | ASTRONAUTICS

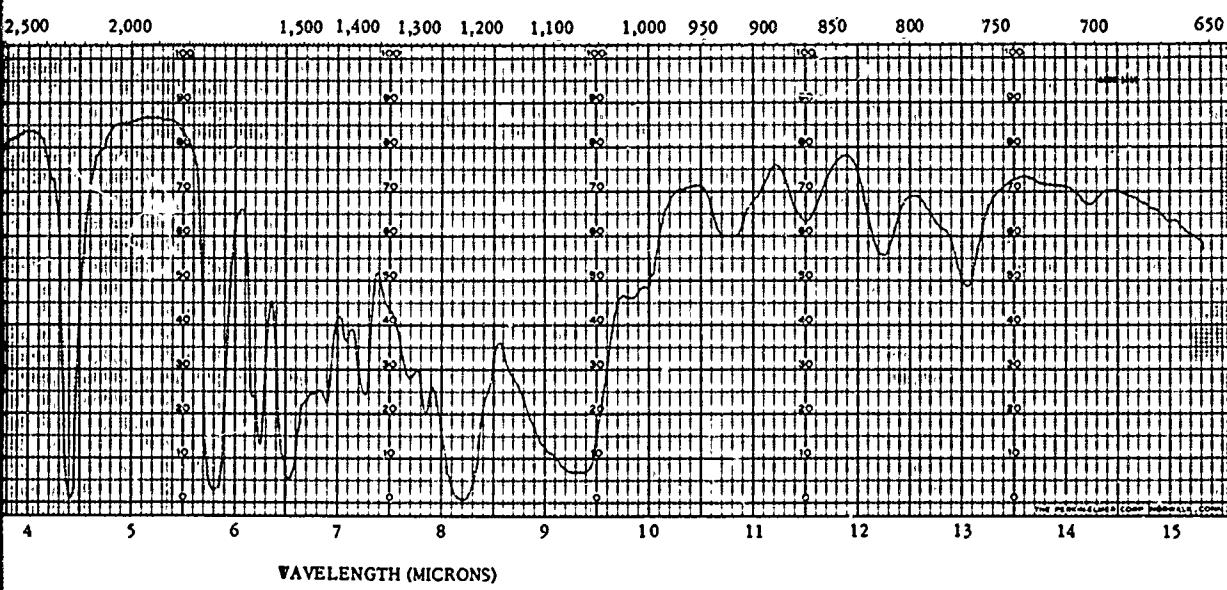


Figure 34. Spectrum of APCO 1219.

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## CONCLUSIONS

1. The Pre-Bond 700 cleaning cycle resulted in the highest strengths at cryogenic temperatures with stainless steel joints bonded with FM-100 and Metlbond 406.
2. An increase in the loading rate from 1,000 to 10,000 ppm at -320° and -423°F will result in approximately a 40% increase in tensile-shear results.
3. Thermal cycling from 78°F to cryogenic temperatures shows no appreciable change in the room-temperature tensile-shear strength of Metlbond 406.
4. Contrary to popular belief, test results indicate that the width of overlap will appreciably affect tensile-shear strength.
5. The use of primers with epoxy-nylon adhesives will lower the tensile-shear strength of the adhesive joints at cryogenic temperatures.
6. The evaluation of Narmco 3170-7133 with stainless steel and titanium adherends at -320° and -423°F resulted in very low strengths when compared to the values obtained at Narmco with 7075-T6 aluminum adherends.
7. No correlation of expansion data and tensile-shear strength at cryogenic temperatures was possible with the adhesive systems evaluated.
8. Butt-tensile and impact tests indicated that the epoxy-nylon unsupported tape adhesives were the best systems for metal-to-metal joints at cryogenic temperature.
9. Pi-tension and plate shear tests at cryogenic temperatures indicated that fiberglass honeycomb core (5.5-5.7 pcf) will normally fail before the epoxy-nylon or filled epoxy-phenolic adhesives.
10. No correlation between molecular structure and adhesive strength at cryogenic temperatures could be obtained because of the variation of adhesives from batch to batch, the proprietary nature of the adhesives, and the variations of degree of cure, length of storage prior to bonding, method of manufacture, etc.

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